ML-TDR-64-297

PYROLYTIC COATING OF CARBON FILAMENTS

November 1964

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7350, Task No. 735002

(Prepared under Contract No. AF 33(657)-11297
by the Advanced Materials Laboratory
Union Carbide Corporation
Carbon Products Division, Lawrenceburg, Tennessee)

UNION CARBIDE

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ADVANCED MATERIALS
LABORATORY

December 4, 1964

To: Report Distribution List

Subject: Contract No. AF 33(657)-11297
Final Report
"Pyrolytic Coating of Carbon Filaments"

Gentlemen:

At the request of the Air Force Materials Laboratory, Research and Technology Division, one copy of the Final Report covering the activity of this laboratory under the subject contract for the period May 15, 1963 to May 15, 1964 is enclosed for your information and retention.

Any questions or suggestions regarding this work should be directed to:

Mr. C. A. Pratt, Jr., - MAMC
Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

Yours very truly,

UNION CARBIDE CORPORATION
Carbon Products Division

Paul G. Lafyatis
Manager, Advanced Materials Laboratory

P. G. Lafyatis
bn

Attachment

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FOREWORD

This report was prepared by the Union Carbide Corporation, Carbon Products Division, under Contract No. AF 33(657)-11297. The contract was initiated under Project No. 7350, "Refractory Inorganic Nonmetallic Materials," Task No. 735002, "Refractory Nonmetallic Materials: Graphitic." The development program was accomplished at the Carbon Products Division, Advanced Materials Laboratory, Lawrenceburg, Tennessee. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division; C. A. Pratt, Jr., was the project engineer.

This report covers the work conducted from 15 May 1963 to 15 May 1964 on "Pyrolytic Coating of Carbon Filaments."

The program was under the direction of Mr. R. M. Bushong. Development work was supervised by Mr. R. C. Stroup and the Investigators were Messrs. K. J. Zeitsch and P. H. Higgs.

ABSTRACT

A continuous process has been developed to coat the individual filaments of graphite yarn with pyrolytic graphite. The pyrolytic coating increased the strength-to-weight ratio of the filaments by a factor of 1.3 and acted as a sizing on the yarn to make weaving easier. Tapes woven from the coated yarn showed a load distribution factor as high as 0.9.

On the basis of these studies, suggestions for extensions of this work are made.

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1. INTRODUCTION

This report covers the one-year program "Research on Unconventional Methods of Processing Unique Graphite Materials." This development effort is a continuation of selected portions of the program for studies leading to the understanding required for development of uniform reproducible carbon-based materials capable of being tailored to meet high-temperature materials requirements in advanced aerospace systems conducted under Contract No. AF 33(616)-6915. The work conducted under Contract No. AF 33(616)-6915 is covered in the various volumes of WADD TR 61-72.

The objective of this program is to develop graphite reinforcing materials with higher strengths by depositing a pyrolytic graphite coating on individual filaments of a graphite yarn through the use of a continuous deposition process. The results of work done under the prior contract[1] demonstrated the feasibility of the process for depositing the pyrolytic coating on the graphite yarn and served as a basis for the initial work done under this contract.

The program was divided into three phases. The first phase work was concerned with the further development of the yarn coating process and the evaluation of the resulting product. In the second phase, selected samples of the coated yarn were woven into tapes for property evaluation. Finally, in phase three, the coated yarn was used as filler for both laminated and macerated fibrous composites.

Manuscript released by authors, October, 1964 for publication as an RTD Technical Report.

2. SUMMARY

A process was developed to deposit uniform pyrolytic graphite coatings on the individual filaments of a multi-filament carbon yarn. The pyrolytic graphite was deposited on the filament by cracking methane as it impinged on the surface of the heated graphite filaments.

Resistance, radiation, and conduction were investigated as the means to heat the yarn to the required deposition temperature. Resistance heating was found to be the most practical. A chamber was then designed in which the heated yarn was surrounded and separated by the coating gas so that all filaments would be coated uniformly.

The tenacity ratio, defined as the ratio of the tenacity after coating to the tenacity before coating, was used to measure coating effectiveness. The tenacity, defined as the pull strength per denier, is proportional to the strength-to-weight ratio of the material. A tenacity ratio greater than 1 indicates that the strength-to-weight ratio of the material has been increased.

Several methods for determining the pull strength of the yarn were evaluated. Measurements with the model X-3 Scott Tester gave the most consistent results.

Tenacity ratios of 1.3 were reproducibly attained under the processing conditions developed.

Other physical properties determined were the electrical resistance, thermal conductivity and the relation of yarn twist-to-pull strength. The pyrolytic graphite coating decreased the electrical resistance and increased the room-temperature thermal conductivity of the yarn. The twist studies indicated that after the yarn has been carbonized, the twist cannot be changed without introducing detrimental effects.

Coated and uncoated yarns were woven into tapes. The coated yarn was found to be well suited for weaving. The coating acted as a sizing which allowed the yarn to move through the loom without fraying. The tapes were evaluated by determining the load distribution factor which is the ratio of the actual longitudinal strength to the theoretical longitudinal (warp) strength. This factor was 0.63 for the tape made from uncoated yarn while it was as high as 0.9 for tapes woven from the pyrolytically coated yarn.

Composite materials were made in both planar and nonplanar forms. For the planar forms, swatches of tape woven from both coated and uncoated yarns were dipped into a resin, stacked to form a laminate and cured under pressure. It was found that the curing pressure had a pronounced effect on the resultant flexural strength of the composite. Although optimum forming conditions were not established, high-strength laminates were fabricated.

The nonplanar composites were made in the form of macerates wherein the fibers were chopped into short sections mixed with a resin and molded into shape by hot pressing. This study revealed that binder level and forming pressure were the key variables. Optimum binder levels and forming pressures were not established, but stronger macerates were made from coated yarn than from uncoated yarn.

3. PROCESS DEVELOPMENT

Under Contract No. AF 33(616)-6915 the feasibility of coating a graphite yarn with pyrolytic graphite was shown.[1] This work served as a basis for the work carried out under the present contract.

The basic requirement for the process is that a heated graphite filament be brought in contact with a carbon-bearing gas at a temperature sufficient to cause deposition of graphite on the filament. Although the pyrolysis reaction is very complex, a complete understanding of the mechanism is not necessary to develop the process.

Process development may be separated into two tasks:

1. Investigation of yarn-heating methods and design of a compatible coating chamber.

2. Study of the effect of significant process variables on coating quality.

The tenacity ratio, which compares the tenacity after coating to the tenacity before coating, was used to measure the effectiveness of the coating.

3.1. Basic Carbon Yarn

The carbonized yarn employed throughout the investigation was a 5-ply material of approximately 2000 denier, with 1-ply twist per inch, and 480 filaments 7 to 10 microns in diameter in each ply.

This yarn was an experimental grade material obtained prior to complete development of the carbonizing process. There was considerable variation from lot to lot of material as well as within each lot. To separate the effect of further carbonization from the effect of the coating, the yarn had to be heated to coating temperatures (1800° to 2200°C) prior to the actual coating process. This heat-treatment was considered an essential and normal part of the process and, except for some of the work in the last phases of investigation, the strength of the coated yarn is compared only with the strength of the material which had been first heat-treated.

3.2. Tenacity and Tenacity Ratio

Tenacity is the standard measure in the textile industry for comparison of the strength of materials. For aerospace applications it is an extremely useful measure that is directly proportioned to the strength-to-weight ratio of the material.

Tenacity (T) is defined by the equation

$$T = \frac{\text{Pull Strength}}{\text{Denier}} \qquad (1)$$

where pull strength is the force in grams required to break the yarn, and denier is the weight of the yarn in grams per 9000 meters of length.

The tenacity ratio (TR) is defined by the equation

$$TR = \frac{T(\text{coated filaments})}{T(\text{uncoated, heat-treated filaments})} \qquad (2)$$

The tenacity ratio, in addition to providing a method for immediate evaluation of any change in the strength-to-weight ratio of the material, gives a conservative estimate of the improvement in tensile strength obtained from the coating.

To eliminate any visual discrepancy in the reporting of results based on the tenacity ratios, these ratios are plotted on logarithm paper thereby giving equal spacing to those ratios below 1 and above 1. A tenacity ratio greater than 1 indicates an improvement in yarn on a strength-to-weight basis.

3.3. Evaluation of Various Heating Methods at Atmospheric Pressures

One of the basic requirements of this process is to heat the yarn to the temperatures required for pyrolytic graphite deposition. Several methods, including resistance heating, radiant heating and conductive heating were evaluated.

3.3.1. Resistance Heating

As an extension of the experience gained under Contract No. AF 33(616)-6915, resistance heating was evaluated first.

In this process, heating is accomplished by passing an electric current through the yarn as it passes between two graphite wheels serving as electrodes. A coating chamber is installed between the electrodes so that while the yarn is heated, it passes through the chamber on a continuous basis. The temperature of the yarn is controlled by adjusting the current flow through it. The coating chamber provides a means of surrounding the yarn with carbon-bearing gases while the yarn is at the selected deposition temperature. In all experiments throughout the program, the carbon-bearing gas was methane diluted with argon.

Regardless of the method of heating used, the design of the coating chamber is an important factor in obtaining a uniform pyrolytic graphite coating on all the filaments in the yarn. Accordingly, several chamber designs were evaluated.

3.3.1.1. Coating Chamber A

The first chamber, illustrated in Figure 1, was based on a design commonly employed in the textile industry for crimping yarns by the

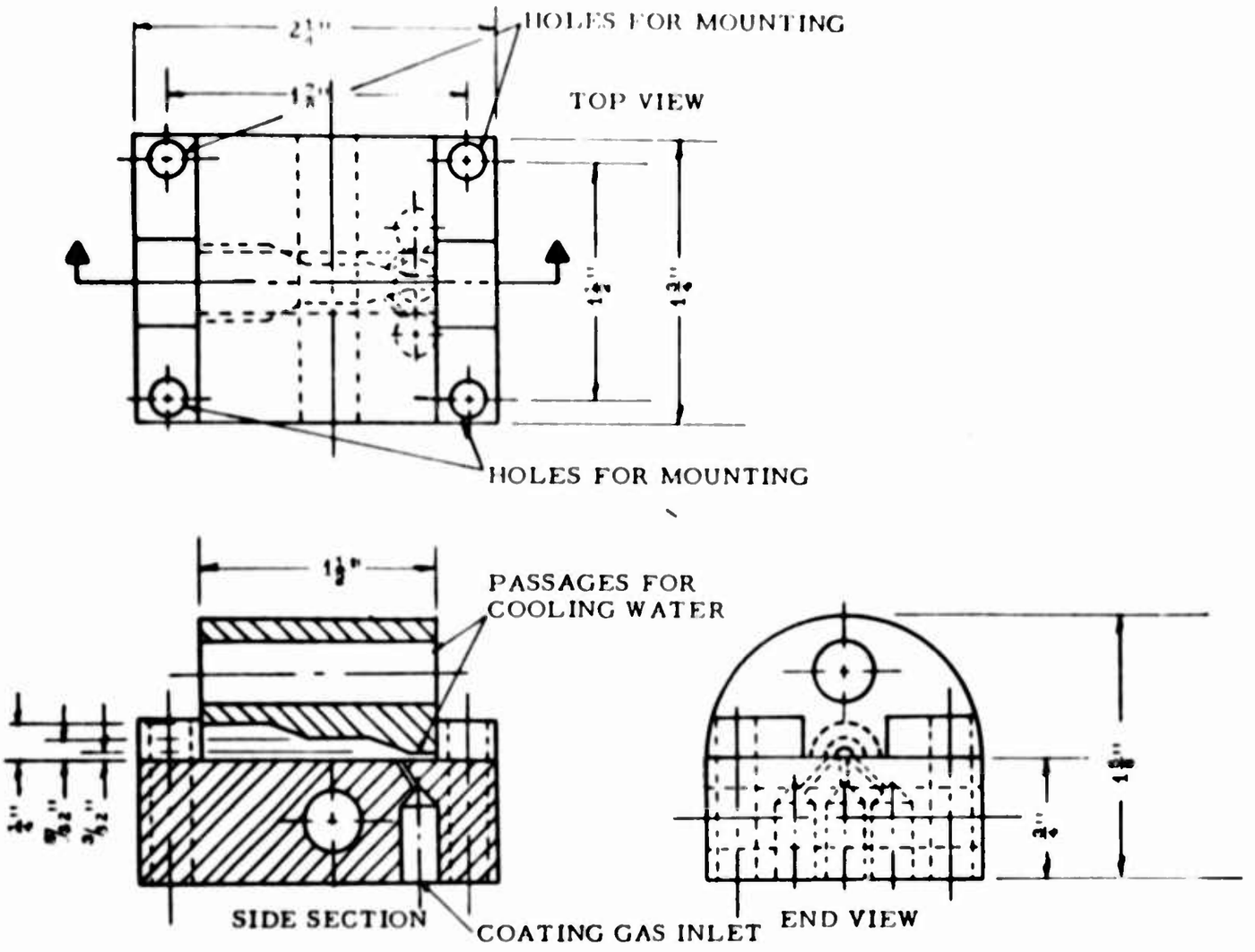

Figure 1. Coating Chamber A

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impingement of high velocity gas. This chamber has provisions for water cooling. The yarn entered the chamber at the smaller of the two openings and moved with the gas flow.

To aid penetration of the coating gas into the mass of the filaments, two nozzles shown in Figure 2, were built. One of these nozzles is placed on the entrance side of the coating chamber and the other on the exit side. Gas is introduced tangentially to the plenum chamber of the nozzle so that a vortex is created. As the yarn passes through the nozzle it is untwisted by the vortex before entering the coating chamber and retwisted to its original form by the other nozzle after leaving the chamber. Both nozzles are provided with argon purge gas passages to provide a protective gas envelope to prevent oxidation outside the nozzle yarn inlets. As the yarn passes through the coating chamber proper,

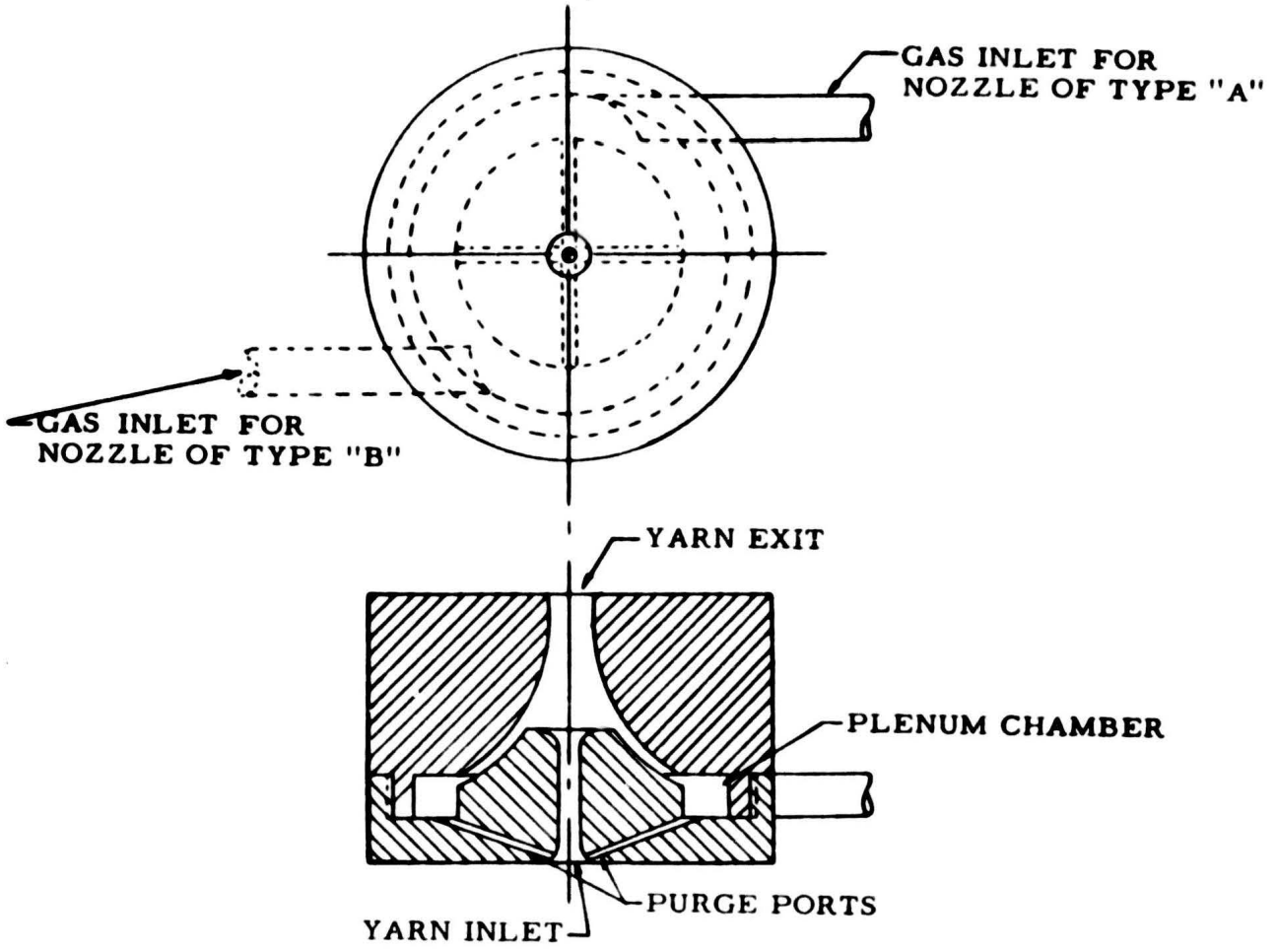

Figure 2. Vortex Nozzles Used to Untwist and Retwist Carbon Yarn

L-980

the untwisted filaments are separated and coated by the impingement of the coating gas mixture. The process schematic is illustrated in Figure 3.

To determine the efficiency of this chamber design, deposition temperatures of 1800° to 2000°C were investigated at methane concentrations of 7 to 25 parts per 100 parts of argon and a constant filament speed of 25 feet per minute. The filament speed is used as the relative measure of residence time of the yarn in the coating chamber. The results are compiled in Figures 4 to 6. Since the ratio of the tenacities of the uncoated and coated material is being plotted, a line corresponding to a tenacity ratio of 1 has been designated as the reference level. Examination of the graphs gives an immediate indication of the improvement or deterioration of the yarn after coating.

This particular design led to the degradation of the tenacity under the conditions studied. The reasons are: 1) oxidation of the yarn occurred between the twisting nozzles and the chamber, 2) the residence time of the yarn within the chamber was too short to allow good coatings

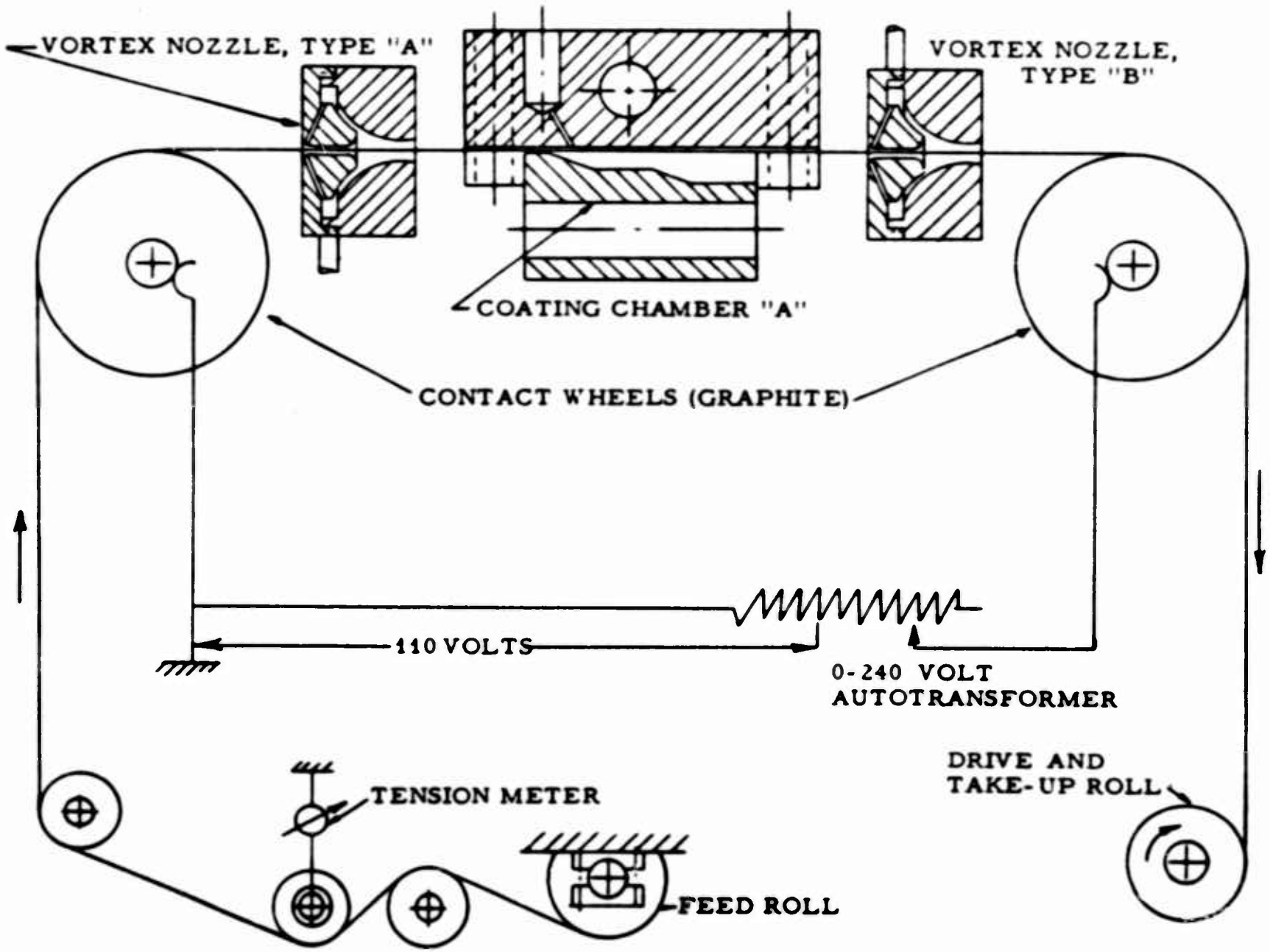

Figure 3. Overall Process Schematic With Chamber A and Vortex Nozzles

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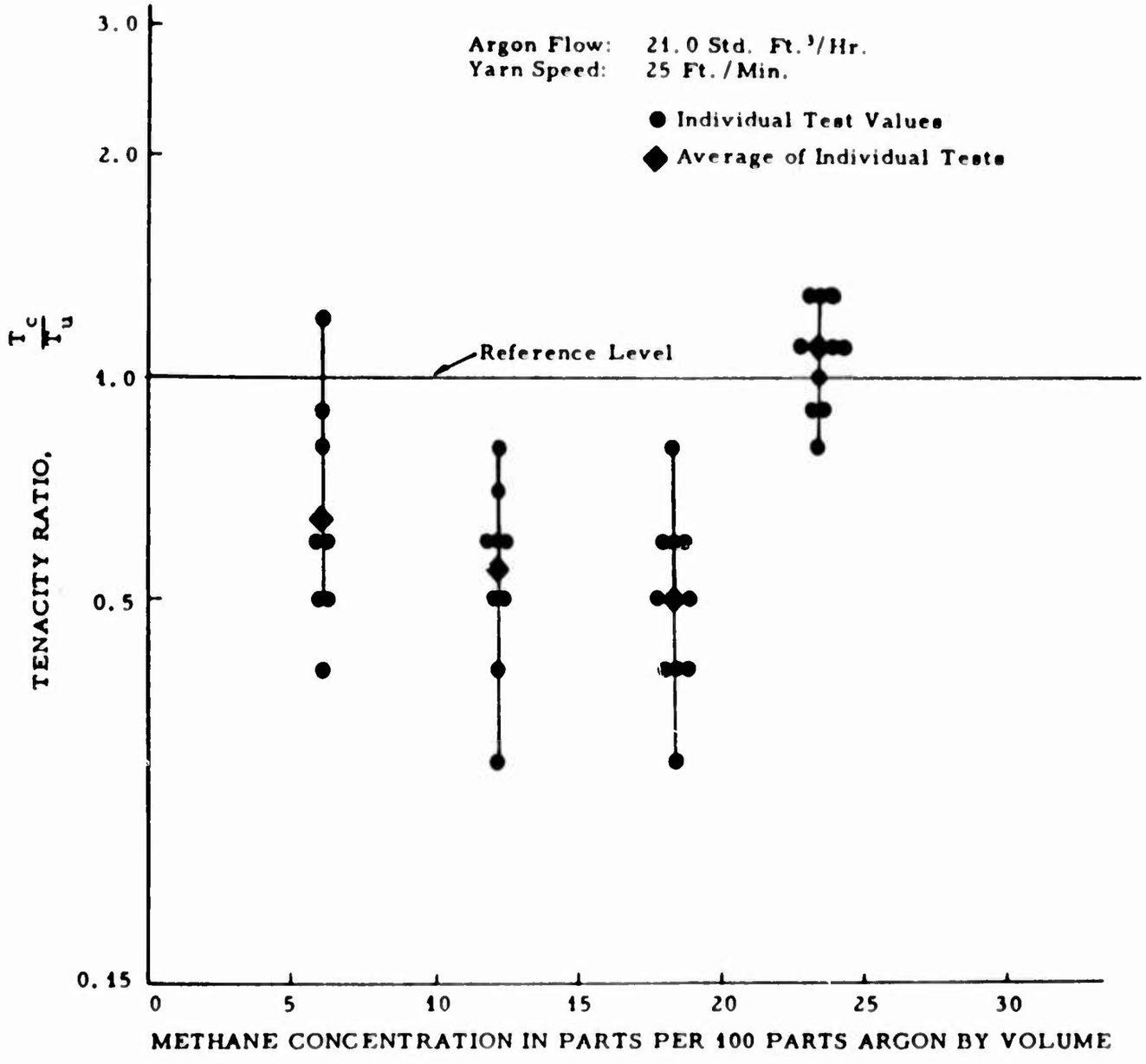

Figure 4. Tenacity Ratio of Yarn Coated in Chamber A at a Deposition Temperature of 1800°C

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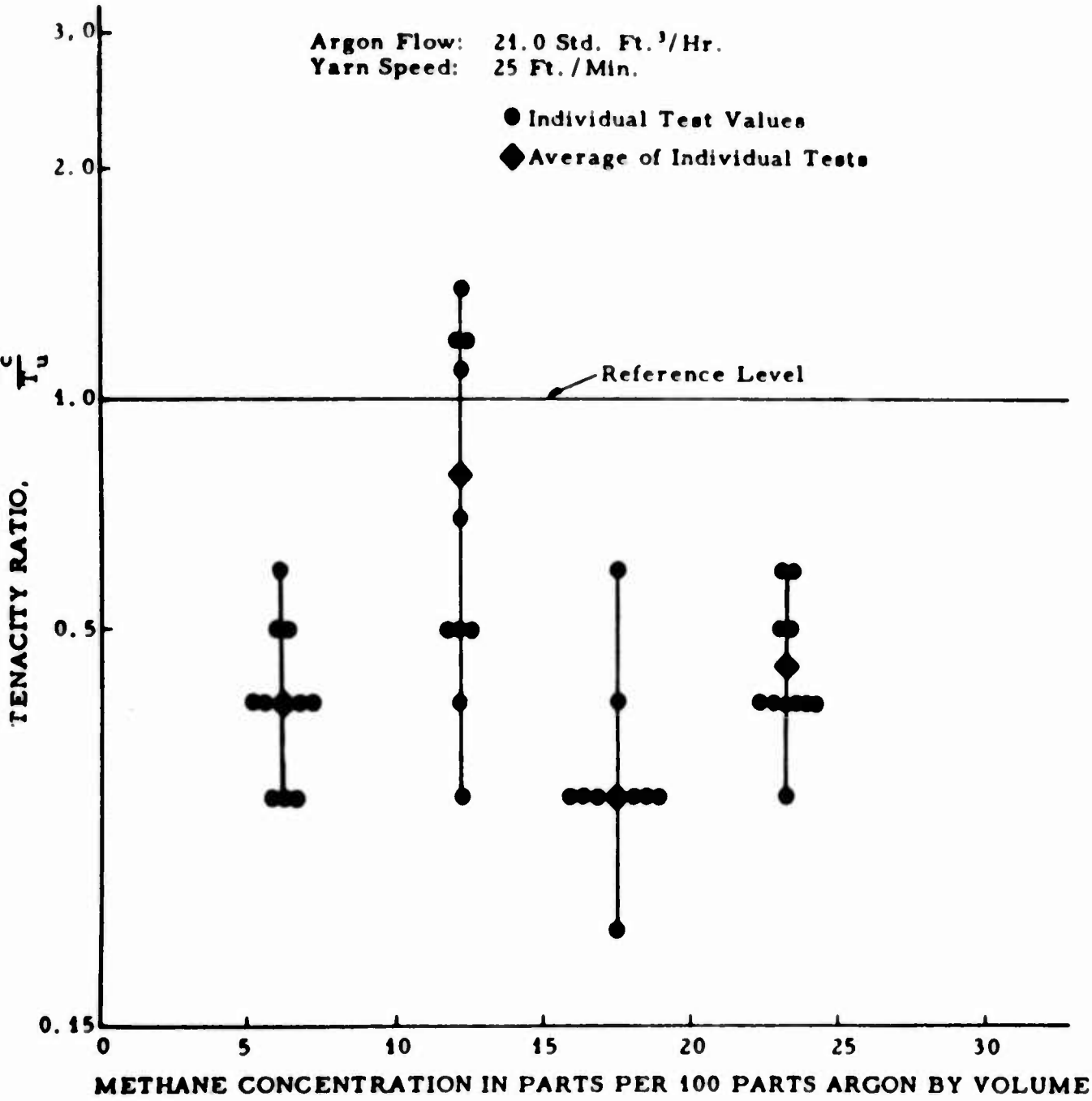

Figure 5. Tenacity Ratio of Yarn Coated in Chamber A at a Deposition Temperature of 1900°C

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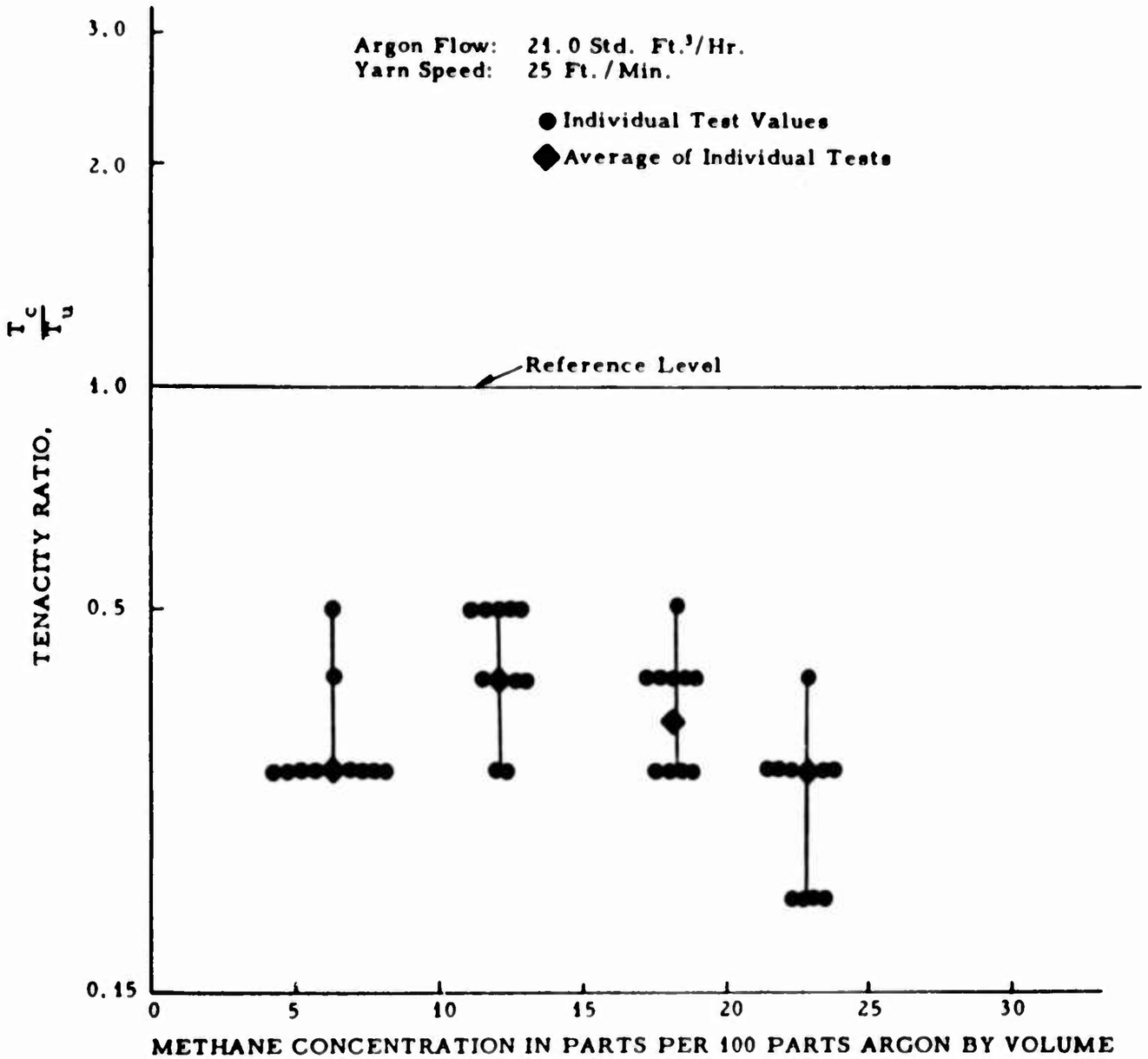

Figure 6. Tenacity Ratio of Yarn Coated in Chamber A at a Deposition Temperature of 2000°C

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Table 1. Data for Figure 4

Yarn Lot No.	UNCOATED YARN	2534
Average Pull Strength, Heat-Treated Form, lbs.:		6.2
Average Denier, Heat-Treated Form, g/9000 m:		2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:		1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
430	5.8	22.5	10	1500	2.8	0.9	0.7
431	11.7	23.8	10	1530	2.9	0.8	0.6
432	17.5	25.0	10	2150	3.0	0.7	0.5
433	23.3	26.3	10	1630	5.2	1.5	1.1

Table 2. Data for Figure 5

Yarn Lot No.	UNCOATED YARN	2534
Average Pull Strength, Heat-Treated Form, lbs.:		6.2
Average Denier, Heat-Treated Form, g/9000 m:		2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:		1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
434	5.8	22.5	10	1450	1.7	0.6	0.4
435	11.7	23.8	10	1520	3.4	1.0	0.8
436	17.5	25.0	10	1570	1.5	0.5	0.3
437	23.3	26.3	10	1630	2.0	0.6	0.5

Table 3. Data for Figure 6

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
438	5.8	22.5	10	1530	1.4	0.4	0.3
439	11.7	23.8	10	1570	2.0	0.5	0.4
440	17.5	25.0	10	1565	1.7	0.6	0.4
441	23.3	26.3	10	1510	1.2	0.3	0.3

to be formed, and 3) the velocity of the coating gases impinging on the yarn was sufficient to fray and weaken it. Decreasing the yarn speed to increase the residence time and also decreasing the coating gas velocity led to more extensive oxidation of the yarn with this coating chamber.

3.3.1.2. Coating Chamber B

Chamber B was designed to overcome the problems encountered with Chamber A. To increase residence time, the chamber was lengthened to approximately three times that of Chamber A. Chamber B is illustrated in Figure 7. Since the distance between the contact wheels was kept constant, the use of the longer chamber also decreased the amount of heated yarn exposed to the atmosphere. The cross-sectional area of the chamber was increased and the gas was introduced at 90° intervals around the yarn. The vortex nozzles were used to separate the filaments.

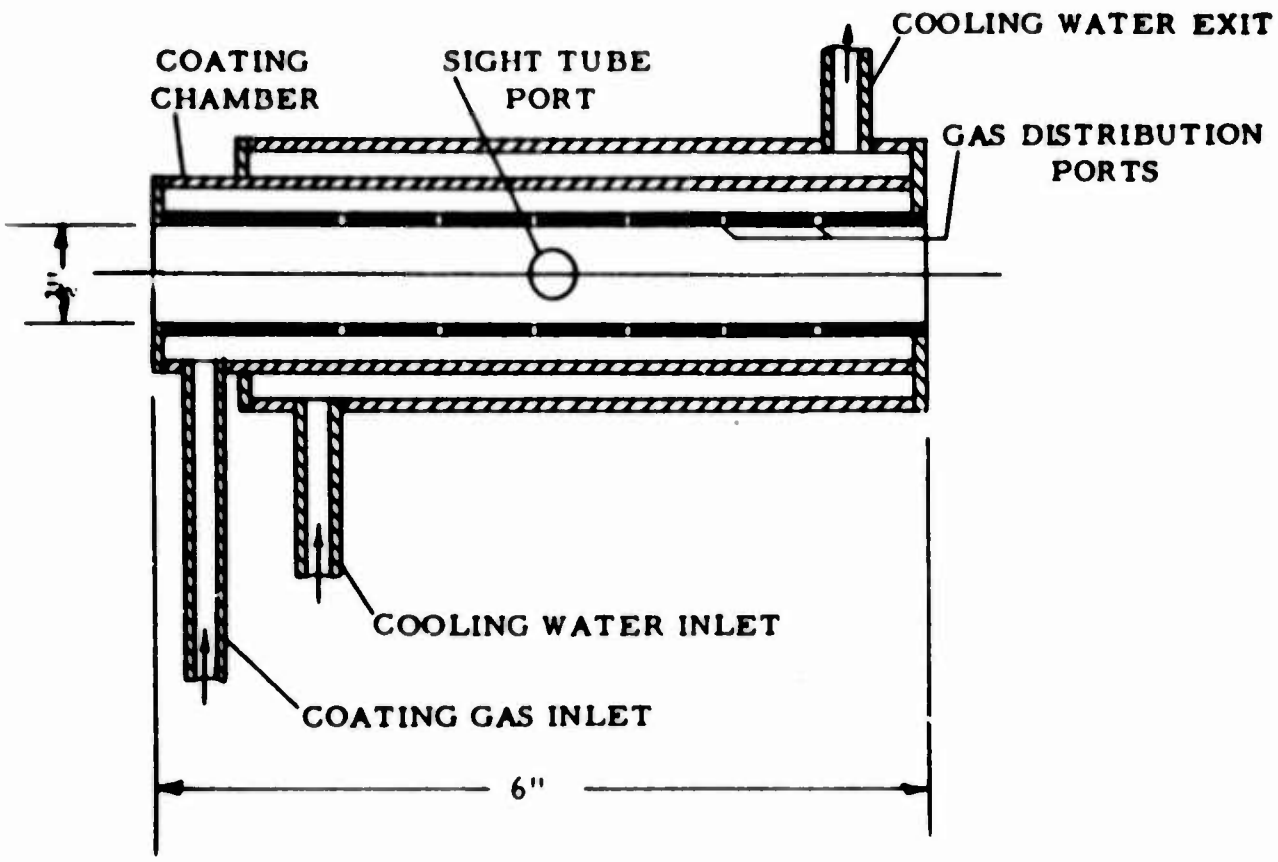

Figure 7. Coating Chamber B

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The results with Chamber B were superior to those with the previous chamber. Figures 8 to 12 show tenacity ratios determined for various deposition temperatures and methane concentrations at a filament speed of 25 feet per minute. Greater penetration was obtained with this chamber and approximately 60 per cent of the filaments were coated with pyrolytic graphite.

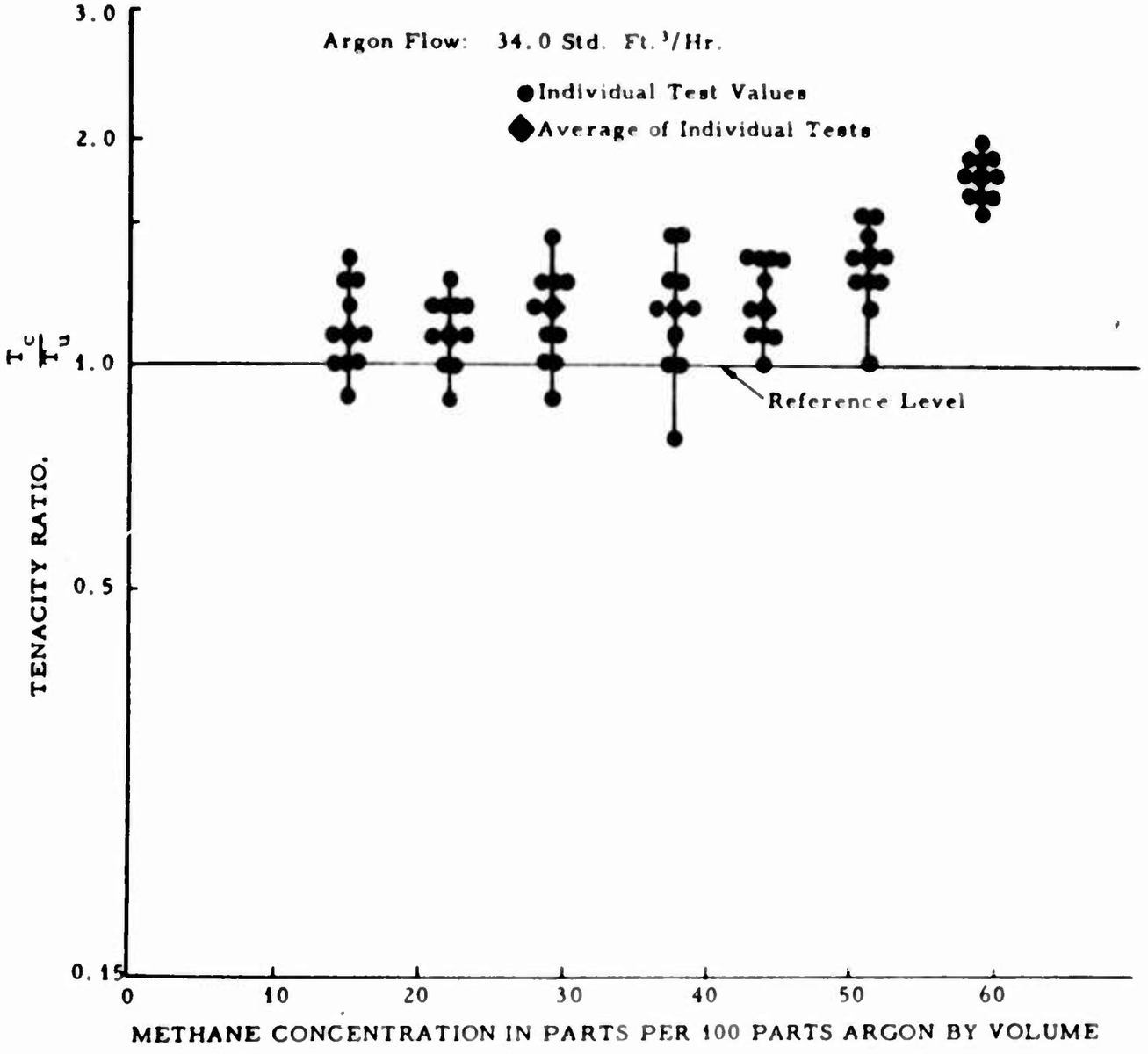


Figure 8. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 1800°C, Series 1: Yarn Speed of 25 Ft./Min.

L-986

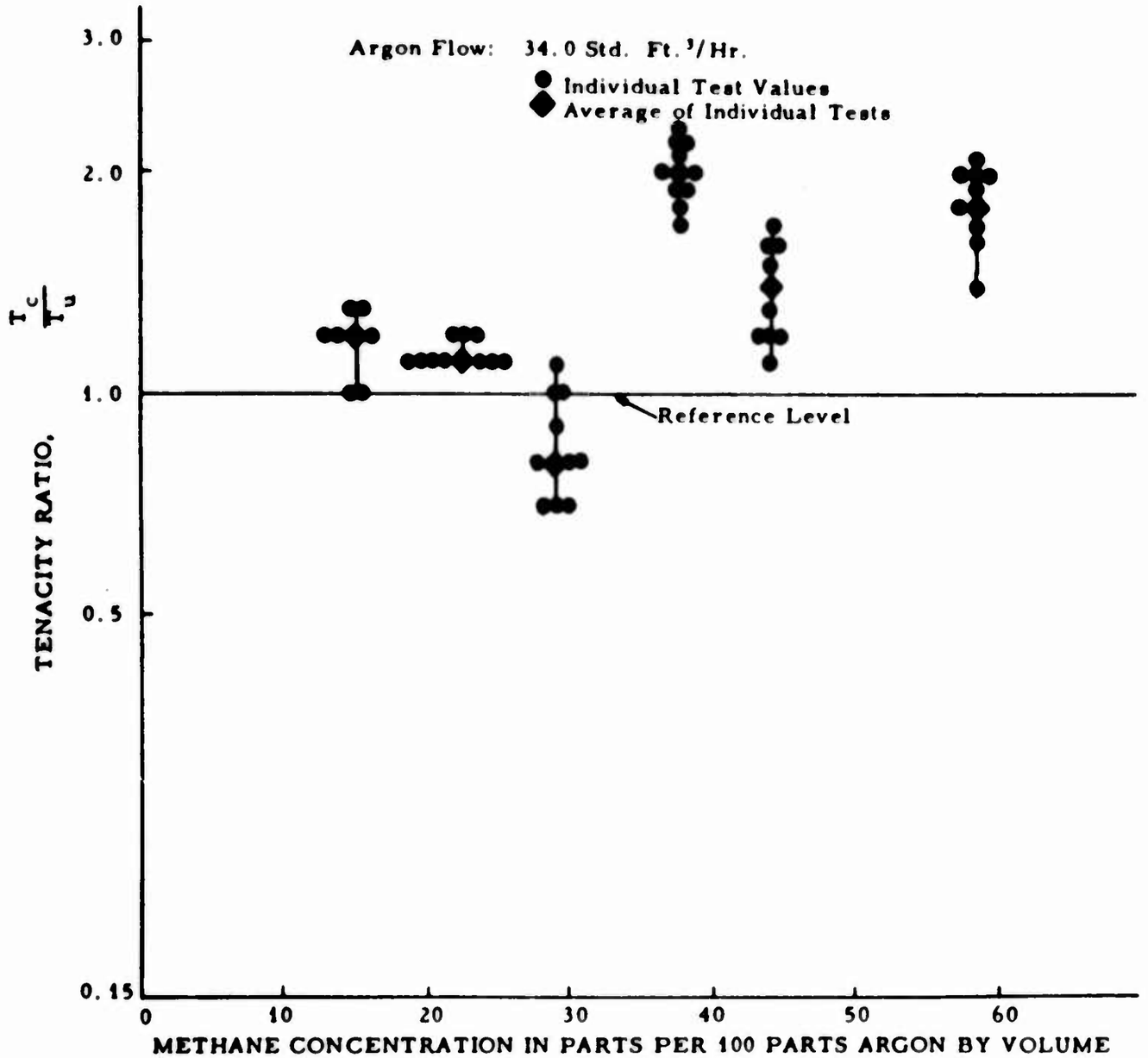


Figure 9. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 1900°C, Series 1: Yarn Speed of 25 Ft./Min.

L-987

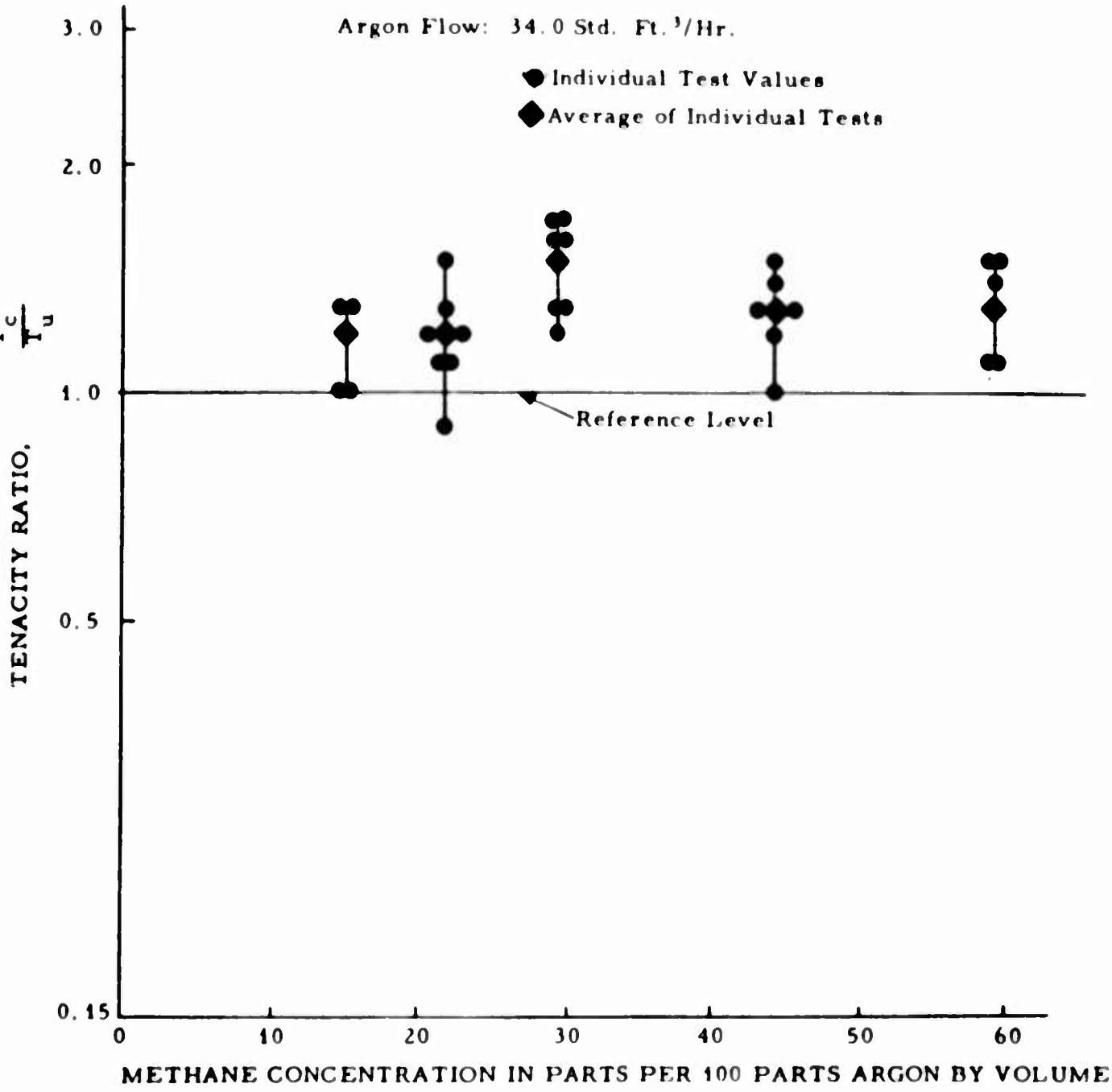


Figure 10. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2000°C, Series 1: Yarn Speed of 25 Ft./Min.

L-988

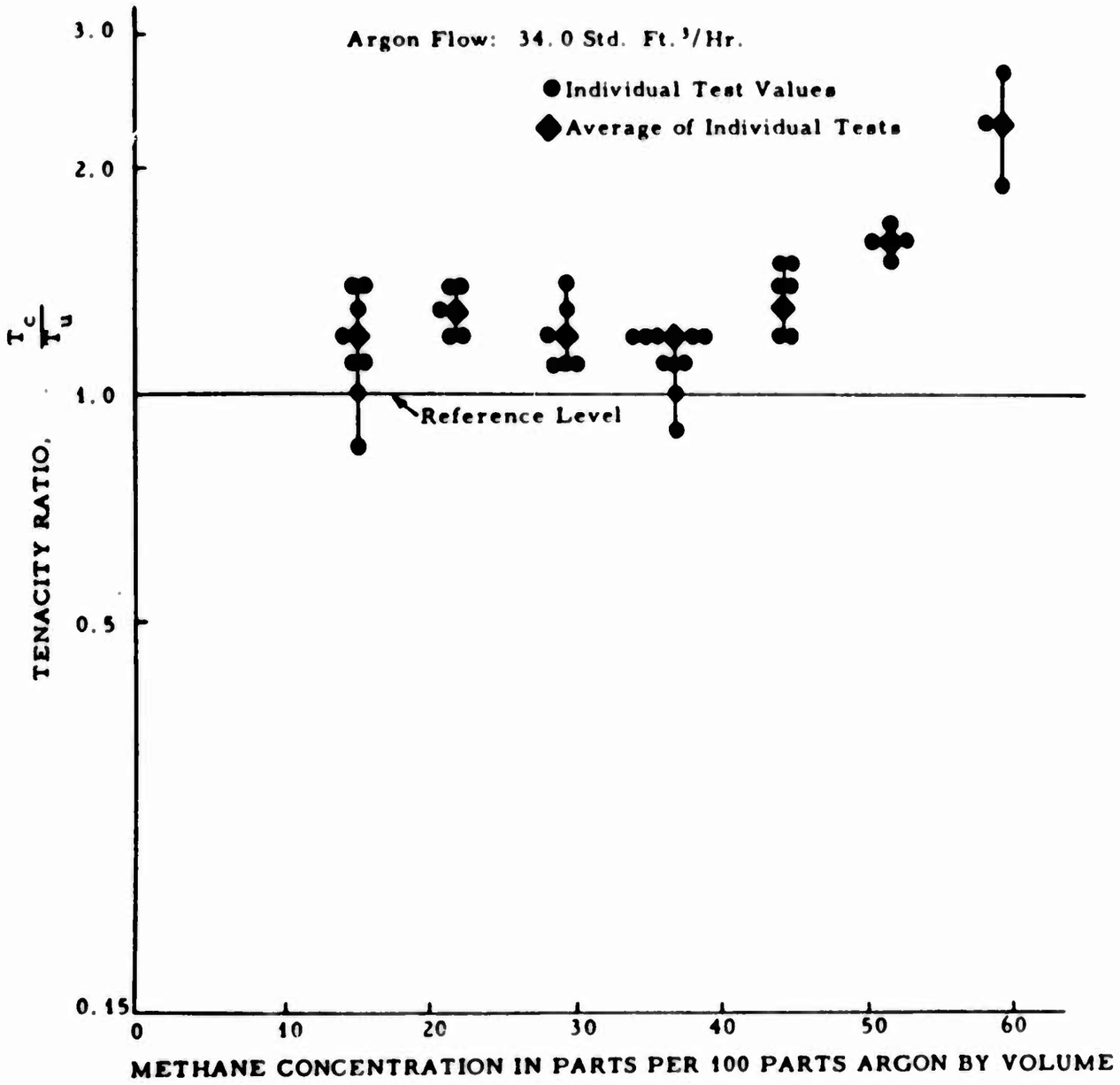


Figure 11. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2100°C, Series 1: Yarn Speed of 25 Ft./Min.

L-989

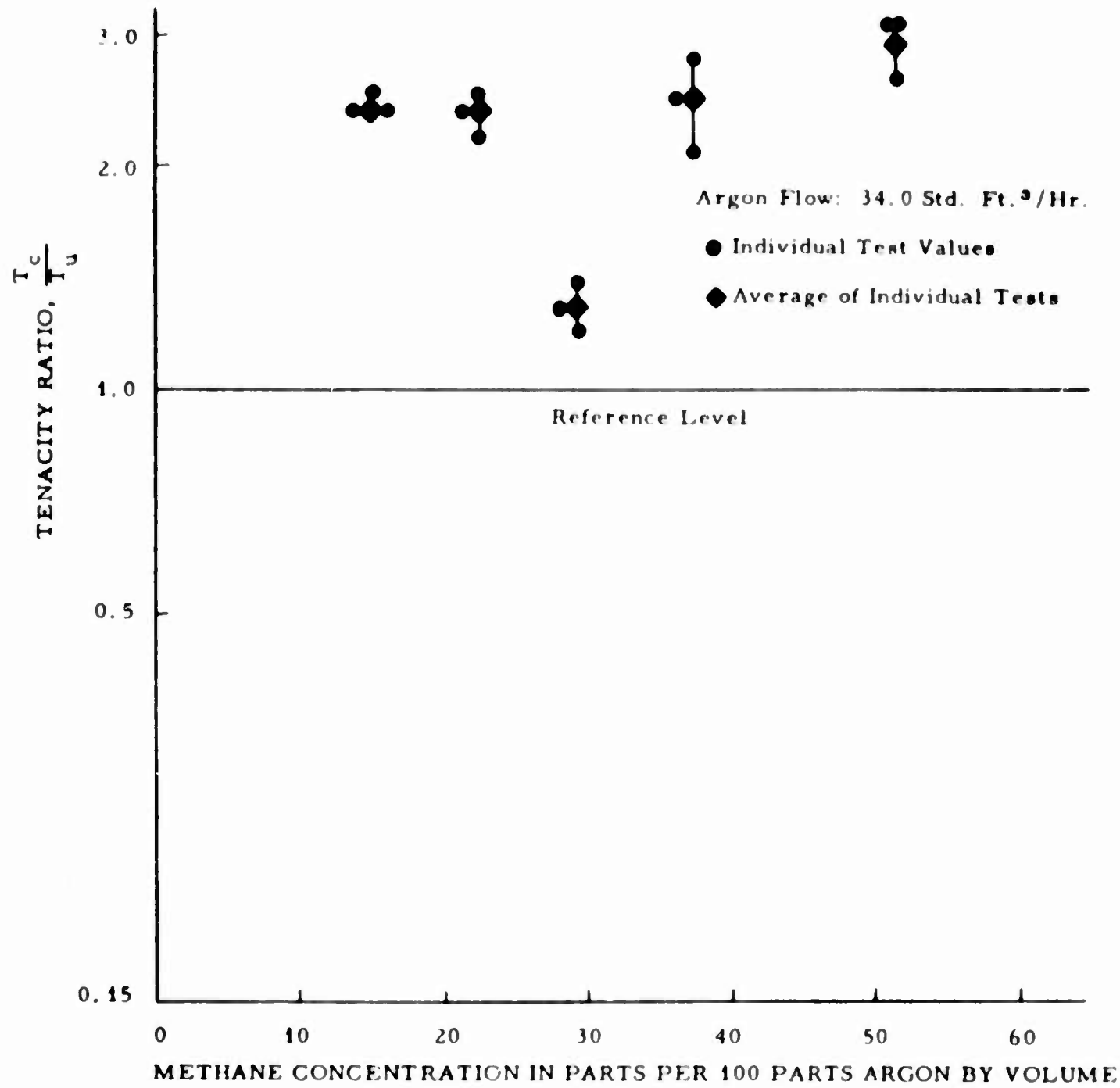


Figure 12. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2200°C, Series 1: Yarn Speed of 25 Ft./Min.

L-990

Table 4. Data for Figure 8

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
442	14.6	38.3	10	2050	6.8	1.5	1.1
443	21.9	41.3	10	2150	7.0	1.5	1.1
444	29.2	44.7	10	2170	7.5	1.6	1.2
445	36.5	46.2	10	2170	7.7	1.6	1.2
446	43.7	48.6	10	2170	7.8	1.6	1.2
447	51.2	51.1	10	2170	8.6	1.8	1.4
448	58.8	53.6	10	1690	8.9	2.4	1.8

Table 5. Data for Figure 9

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
449	14.6	38.3	7	1480	5.1	1.6	1.2
450	21.9	41.3	10	1980	6.5	1.5	1.1
451	29.2	44.7	9	1990	4.9	1.1	0.8
452	36.5	46.2	10	1720	10.0	2.6	2.0
453	43.7	48.6	9	2200	8.7	1.8	1.4
454	51.2	51.1	10	*	12.0	*	*
455	58.8	53.6	10	2160	11.5	2.4	1.8

*Information not available

Table 6. Data for Figure 10

UNCOATED YARN

Average Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
463	14.6	38.3	8	1890	6.5	1.6	1.2
464	21.9	41.3	5	1920	7.3	1.7	1.3
465	29.2	44.7	6	1940	6.8	1.6	1.2
466	36.5	46.2	10	2190	7.3	1.5	1.2
467	43.7	48.6	8	1990	7.7	1.7	1.3
468	51.2	51.1	4	2100	9.7	2.1	1.6
469	58.8	53.6	3	2000	13.4	3.0	2.3

Table 7. Data for Figure 11

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
456	14.6	38.3	4	1910	6.3	1.5	1.2
457	21.9	41.3	7	2040	6.5	1.5	1.2
458	29.2	44.7	7	1990	8.9	2.0	1.5
459	36.5	46.2	6	*	12.4	*	*
460	43.7	48.6	6	2070	7.9	1.7	1.3
461	51.2	51.1	10	*	10.3	*	*
462	58.8	53.6	5	2270	9.1	1.8	1.3

*Information not available

Table 8. Data for Figure 12

Yarn Lot No.	UNCOATED YARN	2534
Average Pull Strength, Heat-Treated Form, lbs.:		6.2
Average Denier, Heat-Treated Form, g/9000 m:		2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:		1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$ /Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
470	14.6	38.3	3	1880	13.2	3.2	2.4
471	21.9	41.3	3	1650	11.4	3.1	2.4
472	29.2	44.7	3	1620	6.0	1.7	1.3
473	36.5	46.2	3	2050	14.8	2.5	2.5
474	43.7	48.6	*	*	*	*	*
475	51.2	51.1	3	2140	18.7	4.0	3.0
476	58.8	53.6	*	*	*	*	*

*Information not available

3.3.1.3. Coating Chamber C

The coatings obtained using Chamber B were sound, indicating that the proper residence time had been determined. Chamber C, shown in Figure 13, was designed to improve the amount of penetration and uniformity of the coating. Deposition temperatures of 1800° to 2200°C and methane concentrations of 7 to 60 parts per 100 parts of argon were investigated. The yarn speed was held constant at 25 ft./min.

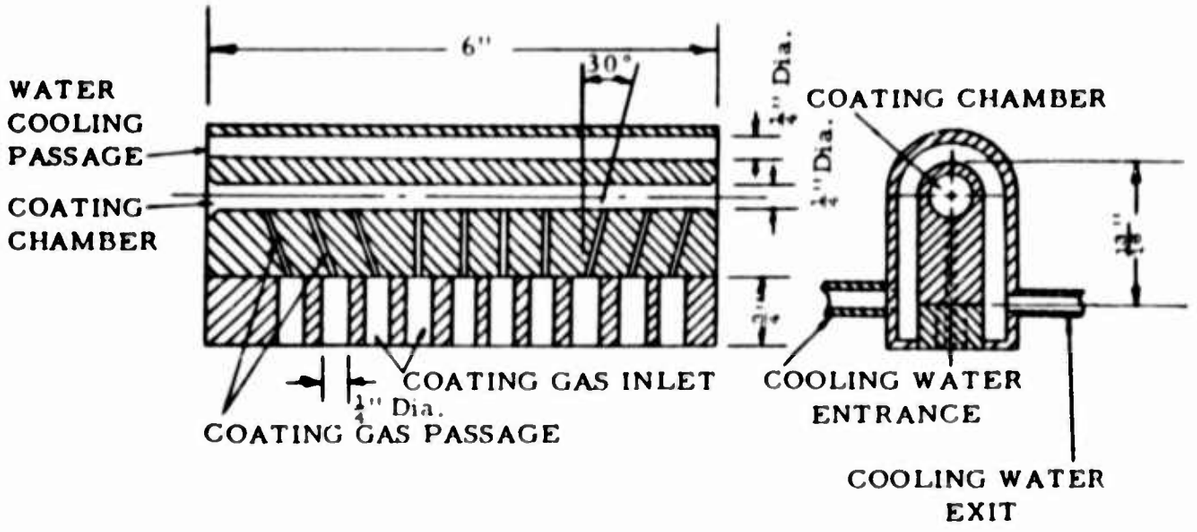


Figure 13. Coating Chamber C

L-991

The results of this evaluation are presented in Figures 14 to 18. Significantly better results were obtained with this chamber than with Chamber A but they were not as good as those obtained with Chamber B. Microscopic examination of the cross section of the coated filaments revealed that the pyrolytic graphite coatings were confined principally to the peripheral filaments leaving approximately 50 per cent of the filaments uncoated. Examination of the action of the yarn in the chamber during the coating processes revealed that yarn bundle was pushed against the side of the chamber by the coating gas flow through the entrance passages. Instead of separating, all the untwisted filaments were actually pressed together at one point making it difficult for the coating gas to penetrate to the interior filaments.

3.3.1.4. Discussion

Analysis of the results obtained with the three chambers showed that the results obtained with Chamber B were superior to those obtained with either Chambers A or C. Chamber B will be used in all succeeding resistance-heating trials. These data obtained with Chamber B are summarized in Figure 19, a relief plot based on average values. The contour

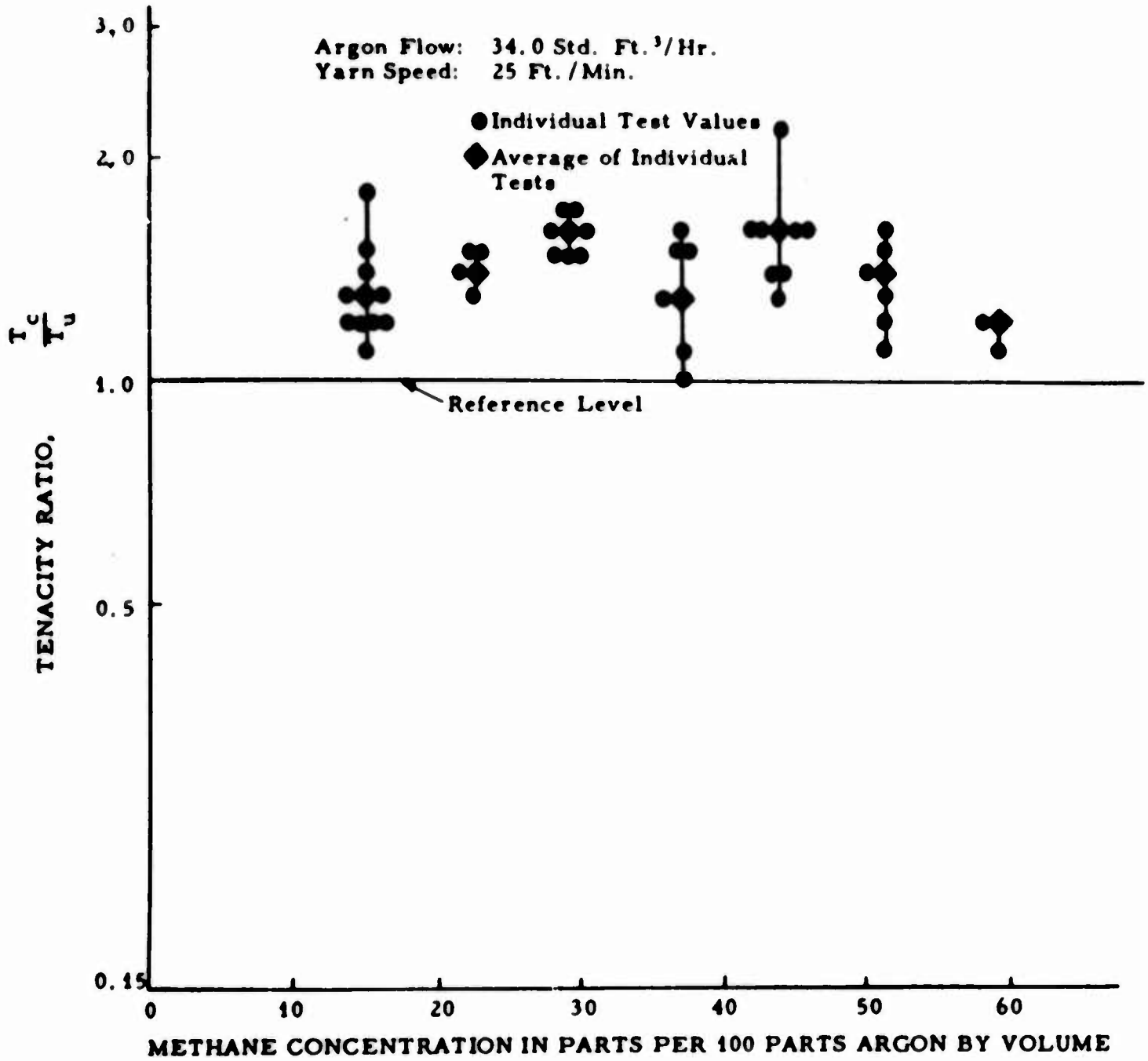


Figure 14. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1800°C

L-992

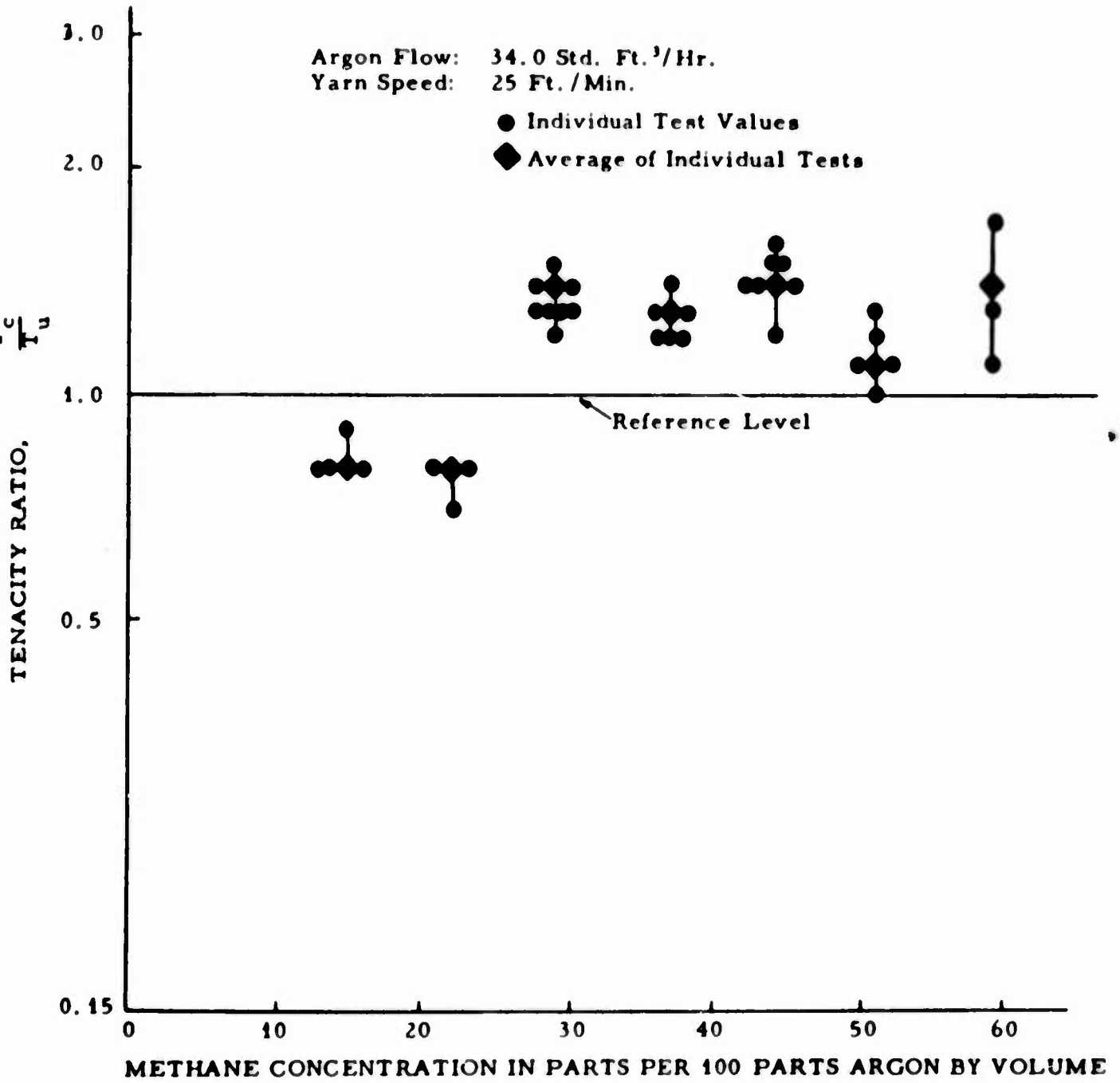


Figure 15. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1900°C

L-993

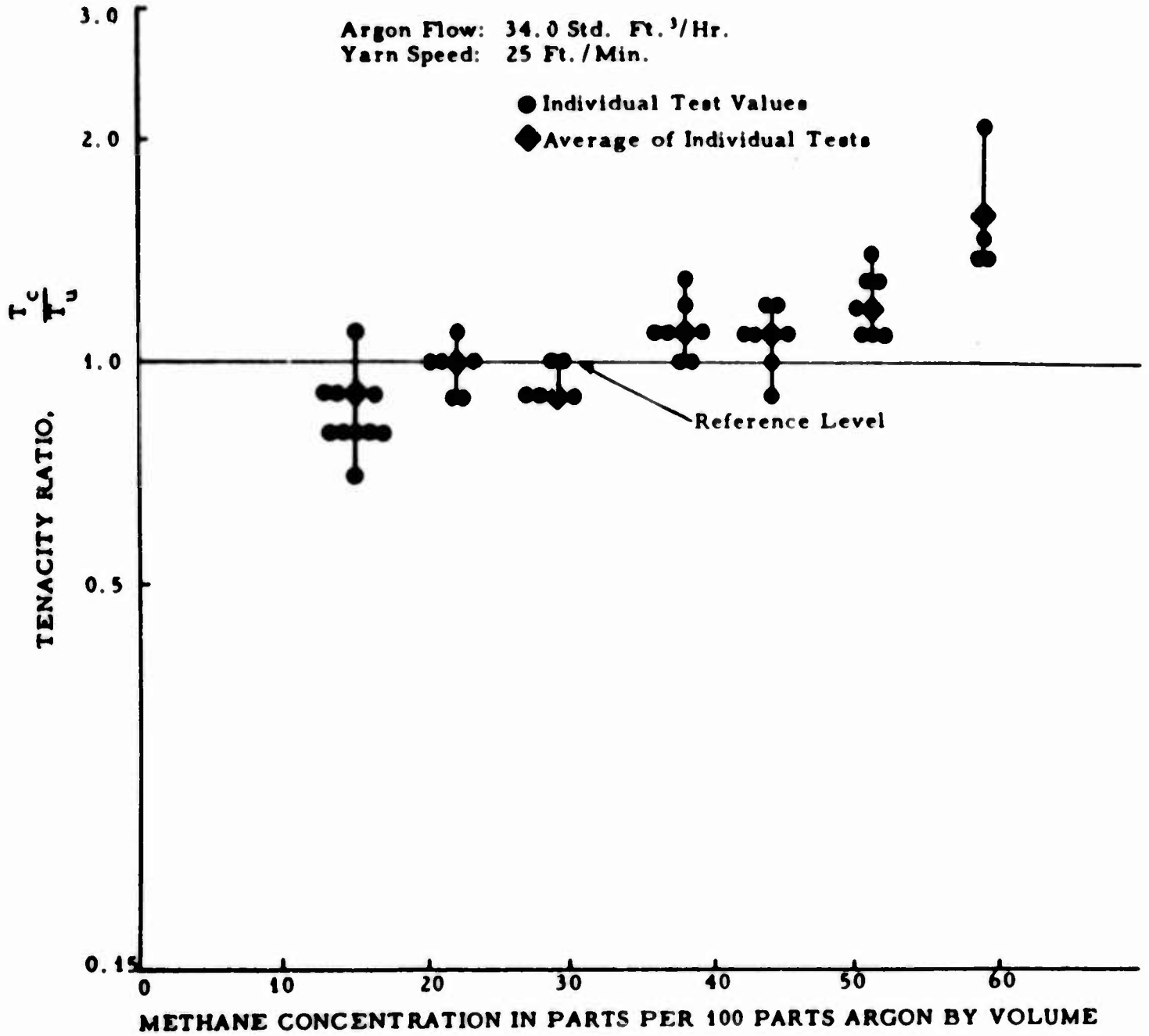


Figure 16. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2000°C

L-991

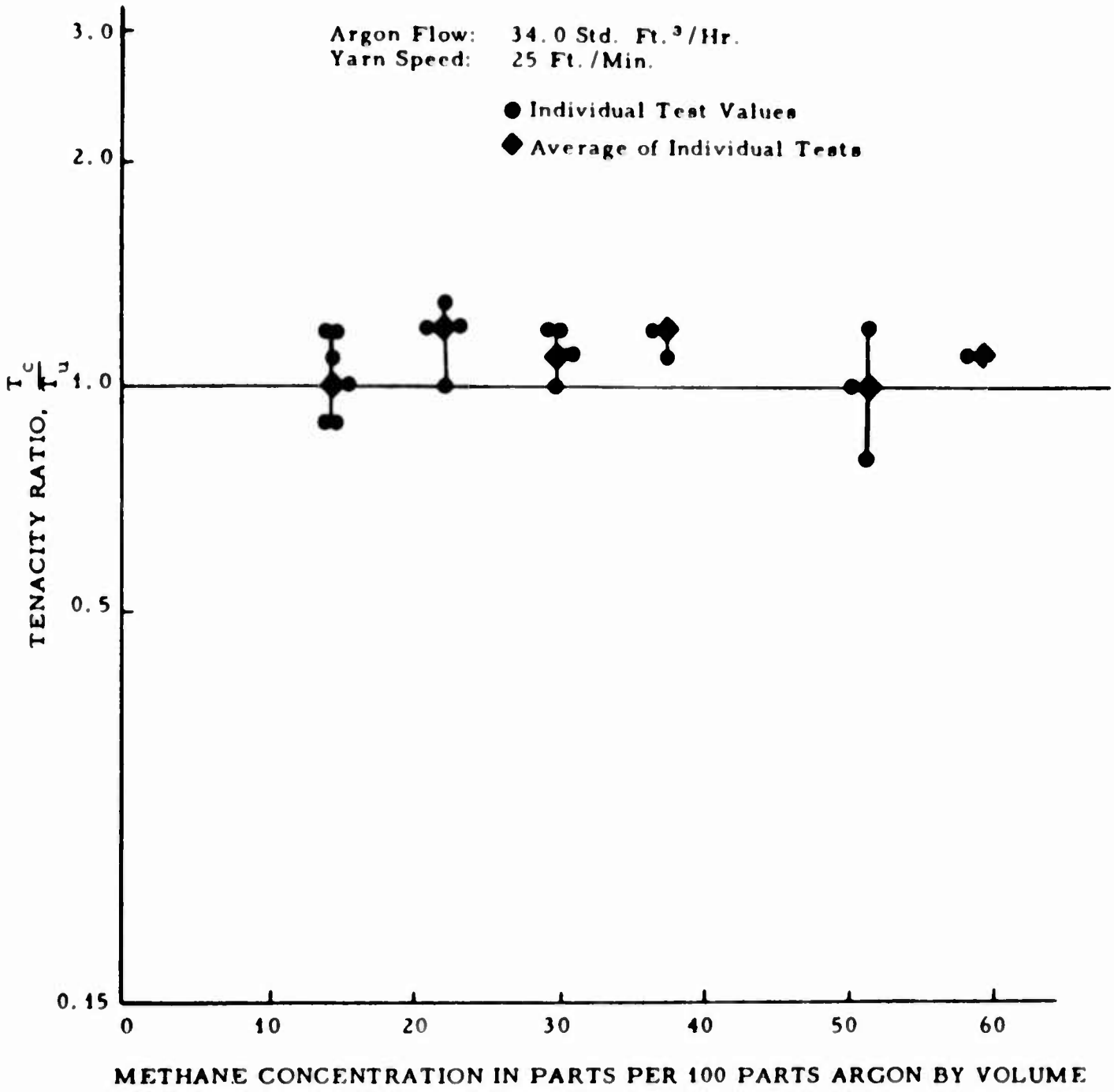


Figure 17. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2100°C

L-995

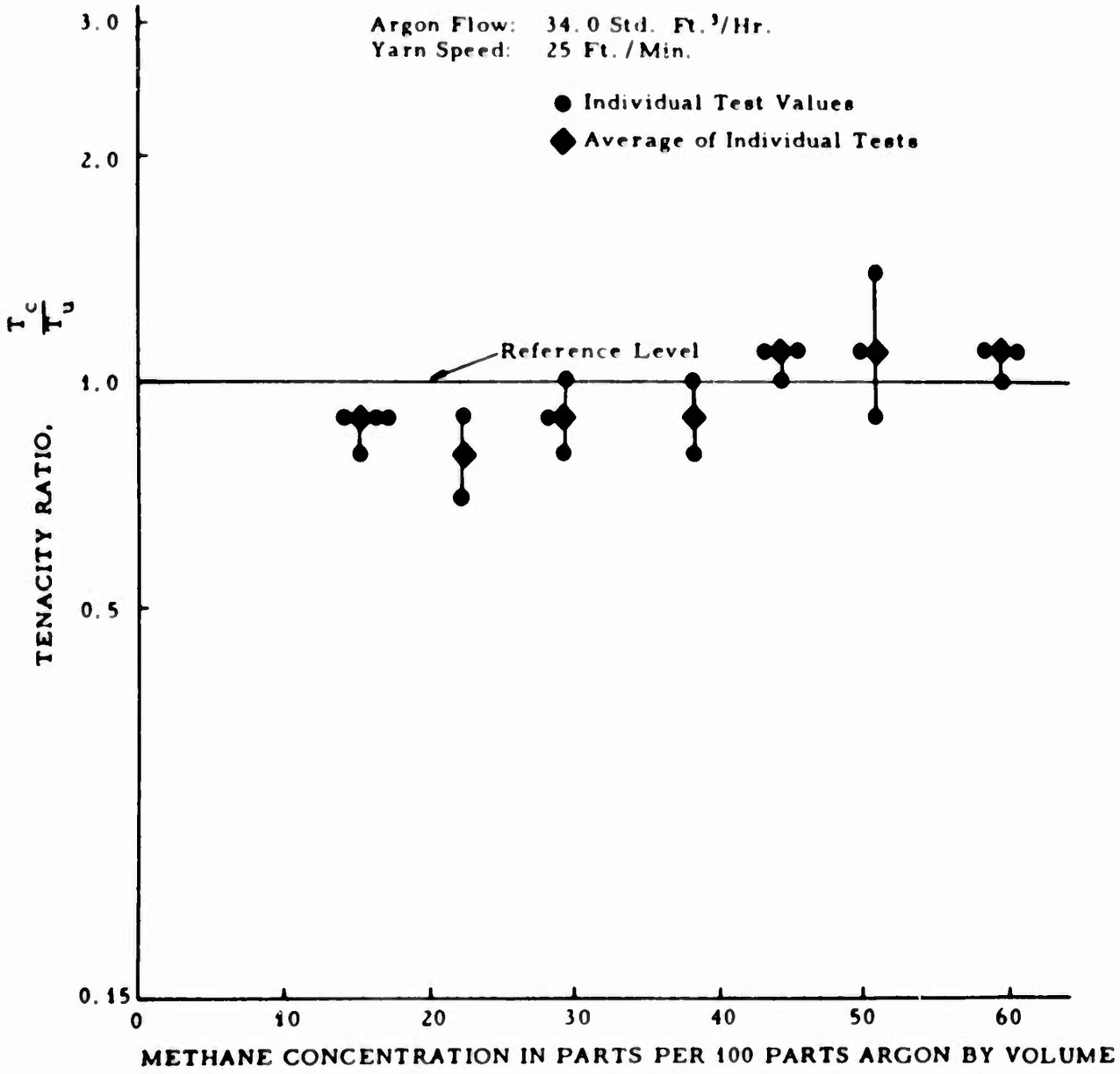


Figure 18. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2200°C

L-996

Table 9. Data for Figure 14

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs. :	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft. /Min

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
480	14.6	38.3	10	2050	8.0	1.8	1.3
481	21.9	41.3	4	2120	8.7	1.9	1.4
482	29.2	44.7	7	2030	9.3	2.1	1.6
483	36.5	46.2	6	2070	8.2	1.8	1.3
484	43.7	48.6	8	1990	9.1	2.1	1.6
485	51.2	51.1	6	1950	8.0	1.9	1.4
486	58.8	53.6	2	1940	6.3	1.5	1.2

Table 10. Data for Figure 15

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs. :	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$ /Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
487	14.6	38.3	4	1930	4.7	1.1	0.8
488	21.9	41.3	3	1830	3.9	1.0	0.8
489	29.2	44.7	8	2030	8.0	1.8	1.4
490	36.5	46.2	6	2310	8.7	1.7	1.3
491	43.7	48.6	7	2060	8.5	1.9	1.4
492	51.2	51.1	5	2150	7.3	1.3	1.1
493	58.8	53.6	3	2090	8.3	1.8	1.4

Table 11. Data for Figure 16

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
494	14.6	38.3	10	1990	5.0	1.1	0.9
495	21.9	41.3	6	1910	5.6	1.3	1.0
496	29.2	44.7	5	2120	5.6	1.2	0.9
497	36.5	46.2	7	1950	6.3	1.5	1.1
498	43.7	48.6	7	1890	6.1	1.5	1.1
499	51.2	51.1	8	1980	6.8	1.6	1.2
500	58.8	53.6	4	2160	10.0	2.1	1.6

Table 12. Data for Figure 17

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
501	14.6	38.3	6	2100	6.2	1.3	1.0
502	21.9	41.3	4	2020	6.9	1.6	1.2
503	29.2	44.7	4	2070	6.5	1.4	1.1
504	36.5	46.2	2	2020	6.8	1.5	1.2
505	43.7	48.6	*	*	*	*	*
506	51.2	51.1	3	2140	6.3	1.3	1.0
507	58.8	53.6	2	2100	7.4	1.4	1.1

*Information not available

Table 13. Data for Figure 18

UNCOATED YARN

Yarn Lot No.	2534
Average Pull Strength, Heat-Treated Form, lbs.:	6.2
Average Denier, Heat-Treated Form, g/9000 m:	2040 ± 30
Average Tenacity, Heat-Treated Form, g/denier:	1.3

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
508	14.6	38.3	4	1910	5.1	1.2	0.9
509	21.9	41.3	2	1920	4.5	1.1	0.8
510	29.2	44.7	3	1980	5.3	1.2	0.9
511	36.5	46.2	2	1980	5.0	1.1	0.9
512	43.7	48.6	3	2010	6.3	1.4	1.1
513	51.2	51.1	3	2110	7.1	1.5	1.1
514	58.8	53.6	3	2050	6.3	1.4	1.1

lines of constant tenacity ratio were fitted into the matrix of data points by linear interpolation.

The results in Figure 19 show that the most significant tenacity increases were in areas of high deposition temperature and high methane concentrations. This would indicate that further investigations should be concentrated at even higher temperatures and concentrations; however, conducting the coating process at these higher levels was found to be impractical. The higher deposition temperatures caused increased susceptibility to oxidation and the increased methane concentration caused the deposition of soot on the peripheral filaments.

The result of increasing both temperature and methane concentration would be the formation of thicker coatings. A thicker coating may also be obtained by increasing the residence time of the yarn within the chamber by decreasing the yarn speed. Increasing the residence time could be expected to result in thicker coatings with corresponding tenacity gains provided prolonged exposure to air does not result in appreciable oxidation, and that embrittlement of the filaments does not result from a too-thick coating.

3.3.1.5. Heat-Treating Evaluation

To make an accurate comparison of the results of the chamber evaluations, we used yarn from the same lot of material (No. 2534) as the starting material in all tests. This material had an average tenacity of 1.3 g/denier and had been heated to 1900°C prior to coating. An experiment designed to determine the optimum heat-treating temperature showed that when the yarn was heated to 1900°C it was essentially stable. Heating to higher temperatures only weakened the material, as shown in Figure 20. Once the yarn had been heated to 1900°C, however, reheating alone had little effect on the strength as shown in Figure 21. Since it was apparent that the use of higher temperatures was only detrimental, 1900°C was selected as the standard heat-treatment temperature for all succeeding coating trials.

3.3.1.6. Residence Time Study

To examine the effect of increasing the residence time, a series of experiments were performed at yarn speeds of 25, 21, 17, and 13 ft./min. The original lot of yarn was depleted in the coating chamber evaluation, and a second lot of material (No. 5071) which had an average tenacity of 1.1 g/denier in the heat-treated form was used. In characteristics such as electrical resistance and twist, it was similar to the original lot.

For the coating chamber evaluation, the coating equipment was mounted open to the room atmosphere and the gas sheath from the coating chamber and twisting nozzles provided oxidation protection for the yarn while it was heated between the contact wheels. For the residence time

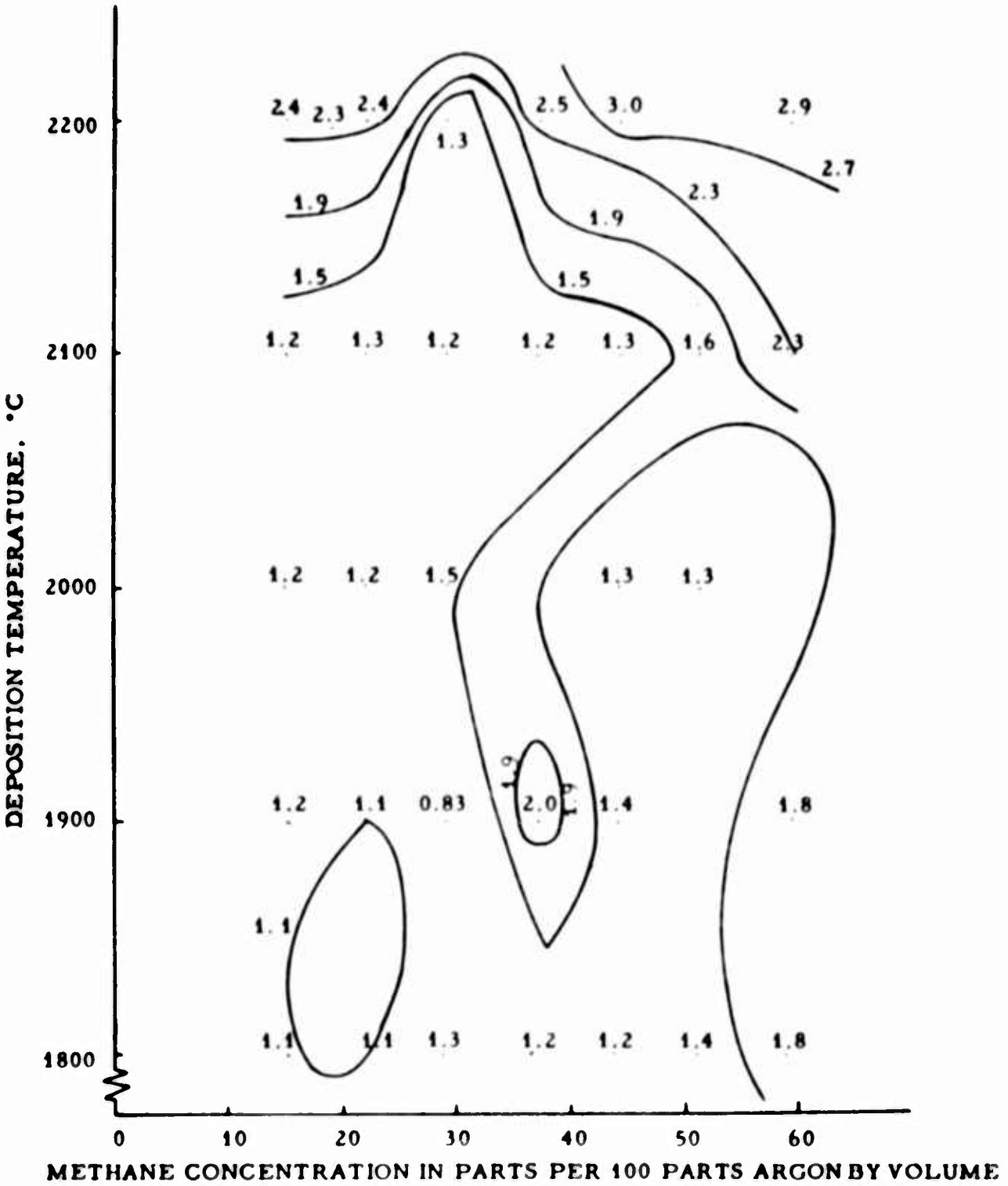


Figure 19. Performance Characteristics of Chamber C, Relief Plot of the Tenacity Ratio as a Function of Methane Concentration and Deposition Temperature

L-997

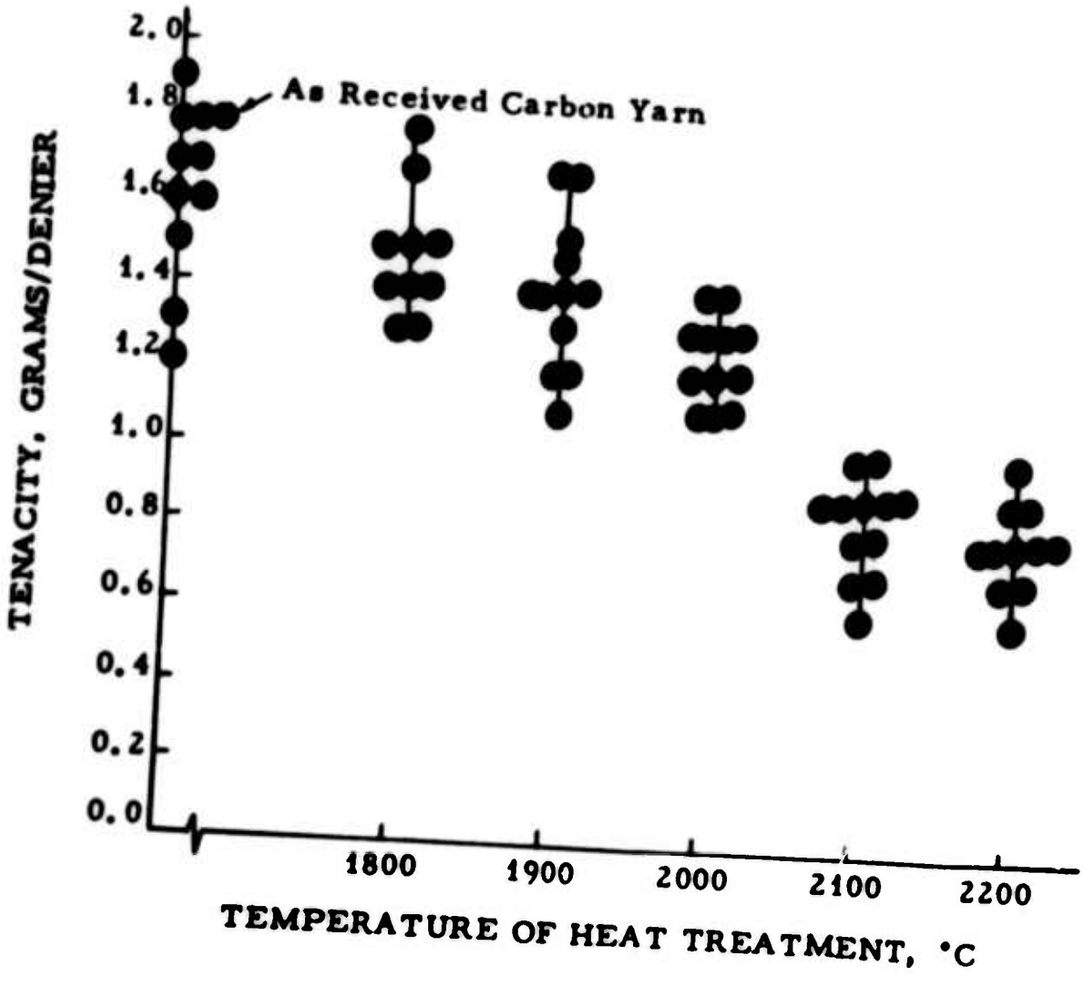


Figure 20. Effect of Heat Treatment on the Tenacity of Carbon Yarns

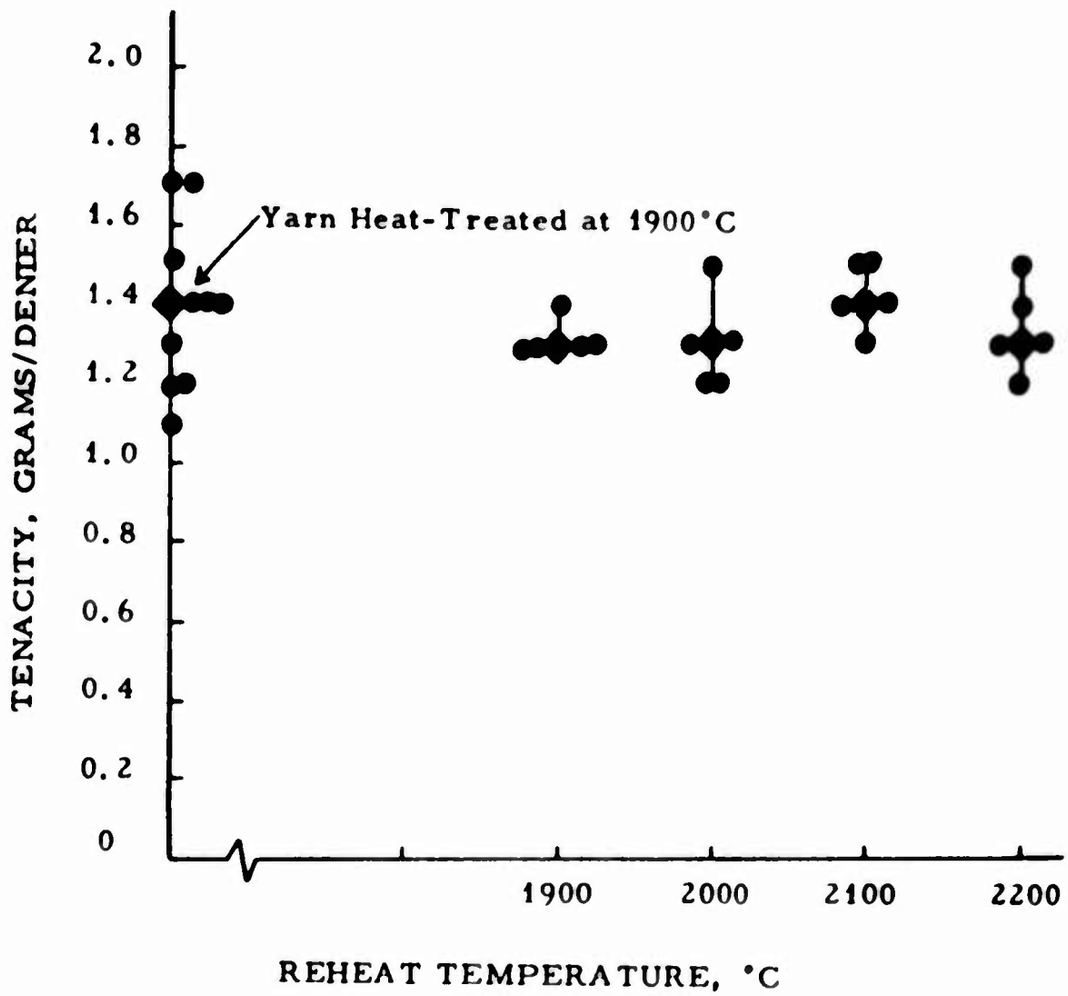


Figure 21. Effect of Reheating Heat-Treated Yarn in an Argon Atmosphere

L-999

Table 14. Data for Figure 20

Yarn Lot No.	UNCOATED YARN Yarn Speed: 25 Ft. /Min.			2534	
Expt. No.	Heat Treat Temperature, °C	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier
400	As Received	10	2790	10.0	1.6
401	1800	9	2140	7.0	1.5
402	1900	10	2040	6.2	1.4
403	2000	10	1845	5.0	1.2
404	2100	10	1810	3.4	0.9
405	2200	10	1860	3.3	0.8

Table 15. Data for Figure 21

Yarn Lot No.	UNCOATED YARN Yarn Speed: 25 Ft. /Min.			2534	
Expt. No.	Reheat Temperature, °C	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier
406	1900	5	2070	6.0	1.3
407	2000	5	2040	5.9	1.3
408	2100	5	2020	6.3	1.4
409	2200	5	2030	5.9	1.3

evaluation, the equipment was installed in a transite enclosure with argon continually flushed around the equipment. This was to reduce the amount of oxygen in the gas sheath around the yarn.

The results of these trials, using Chamber B, are shown in Figures 22 to 41 and are much less definitive than those obtained in the coating chamber trials using the original lot of yarn. Figure 42 is a relief plot of the tenacity ratio of the second lot of yarn at the same speed and coating conditions as the first lot of material shown in Figure 19. In Figure 42 the contour interval is 0.2 g/denier and it is evident that the trend toward increasing tenacity with higher methane concentration and higher temperatures is much less pronounced than with the original starting material. The reason for this was not clear but was believed to be due to some undetermined difference in the two starting materials.

Based on these trials, it appears that within the limits studied residence time has little effect on the tenacity. Even at the highest filament speed, 25 ft./min., sufficient time was available for deposition to take place. Increasing the residence time by decreasing the filament speed resulted in increasing the thickness of the coating which tended to embrittle the yarn. This embrittlement plus further oxidation which occurred at the slower speeds accounts for the low tenacities which were obtained. At the lower speeds, the destructive effects of oxidation and embrittlement greatly outweigh any benefits that might arise from the increased residence time. The next effort was aimed at eliminating oxidation.

3.3.2. Radiant Heating

During the trials with resistance heating, it became apparent that there were two potential disadvantages to using this method of heating.

1. A 2-inch length of yarn at either end of the coating chamber (between the chamber and the graphite electrodes) is incompletely sheathed by the coating gas and is subject to oxidation.

2. As the yarn leaves one contact wheel and approaches the other, visible arcing occurs between the yarn and the contact wheel and it is likely there is additional arcing within the yarn as well.

Both of these conditions could change the yarn structure with possible harmful effects on yarn strength and flexibility. Microscopic examination has disclosed a tendency for the outer yarn filaments to be reduced in diameter after processing by resistance heating which constitutes further evidence that some oxidation occurs during the process.

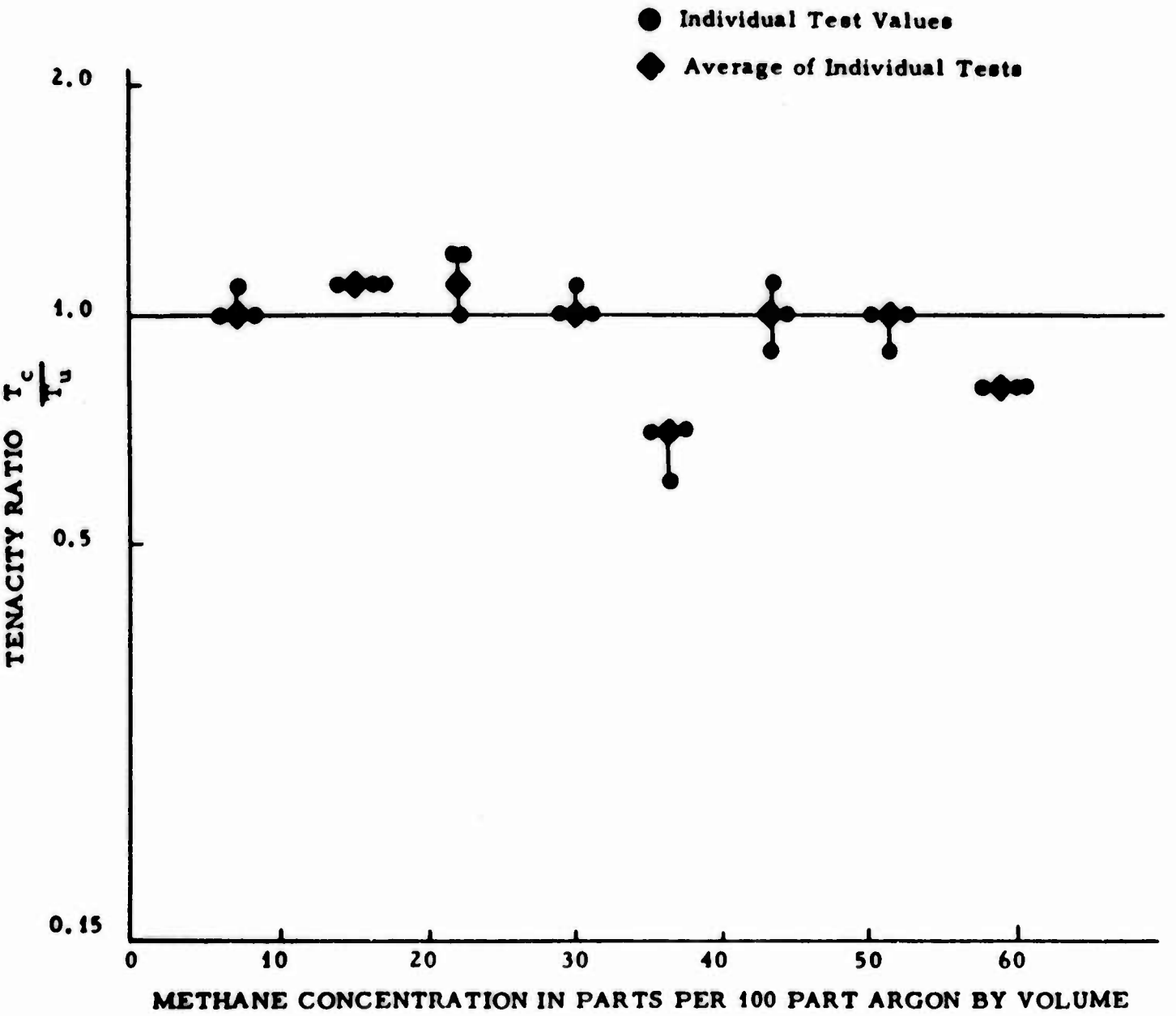


Figure 22. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 1800°C, Series 2: Yarn Speed 25 Ft./Min.

L-1000

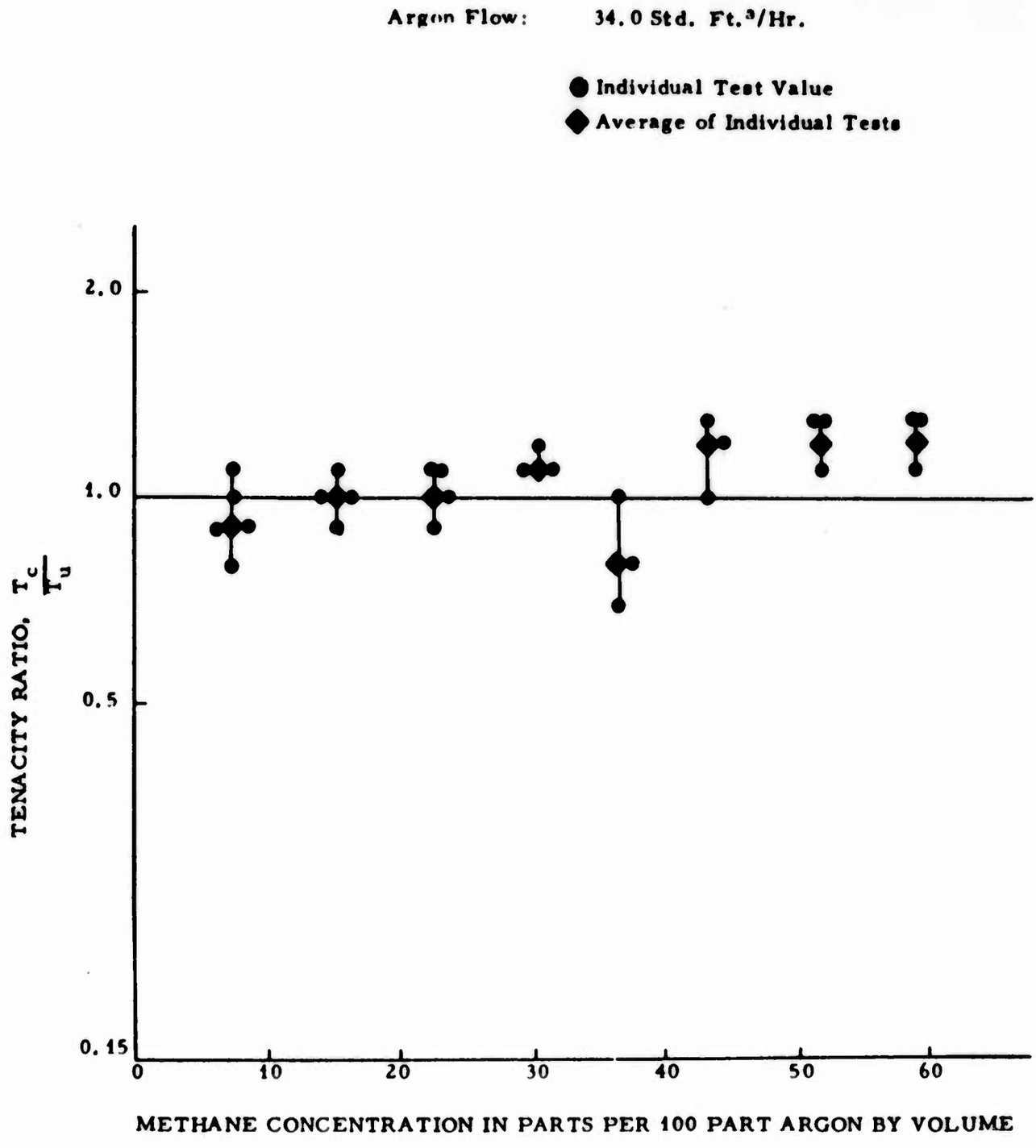


Figure 23. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 1900°C, Series 2: Yarn Speed of 25 Ft./Min.

L-1001

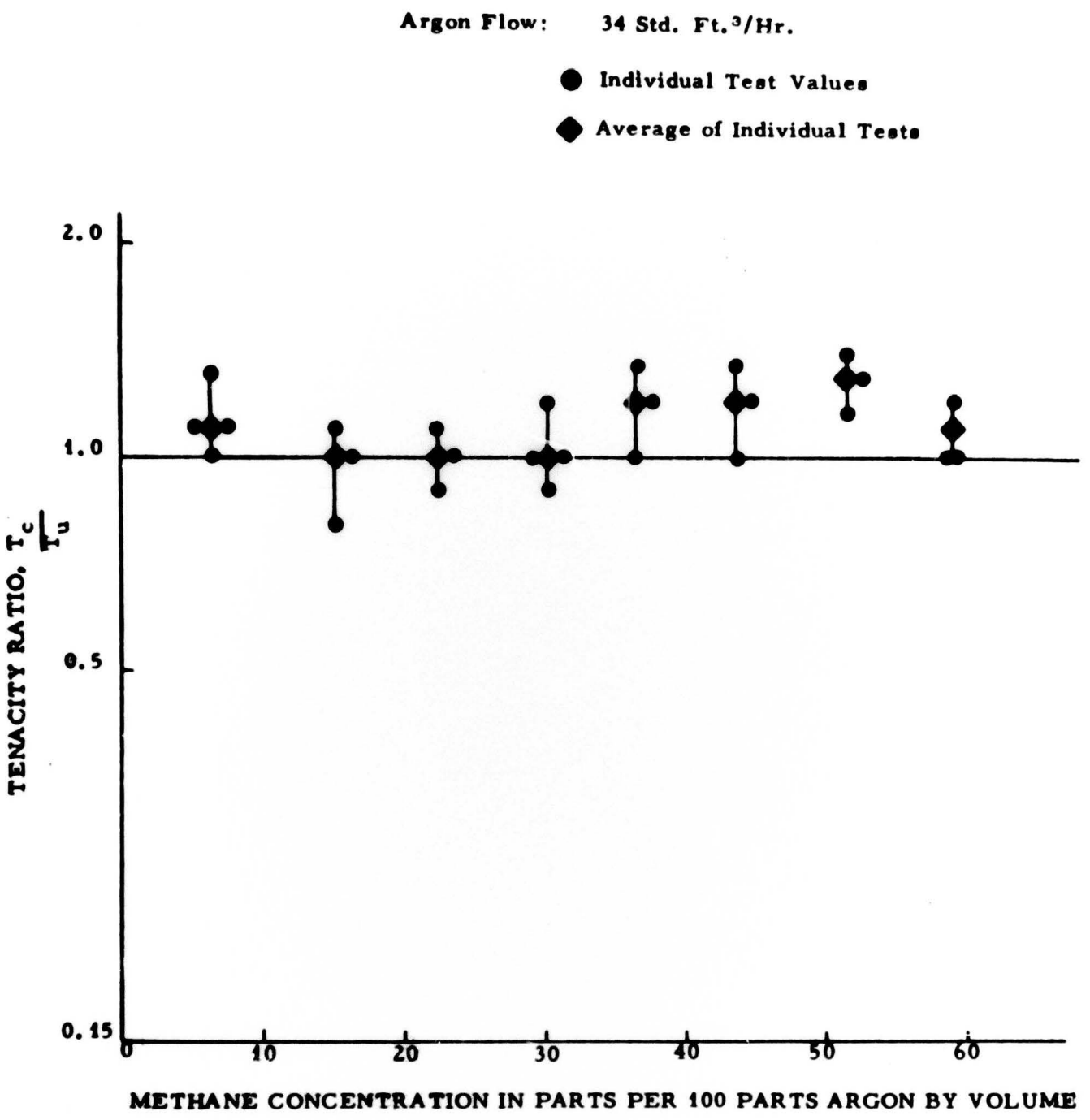


Figure 24. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2000°C, Series 2: Yarn Speed of 25 Ft./Min.

L-1002

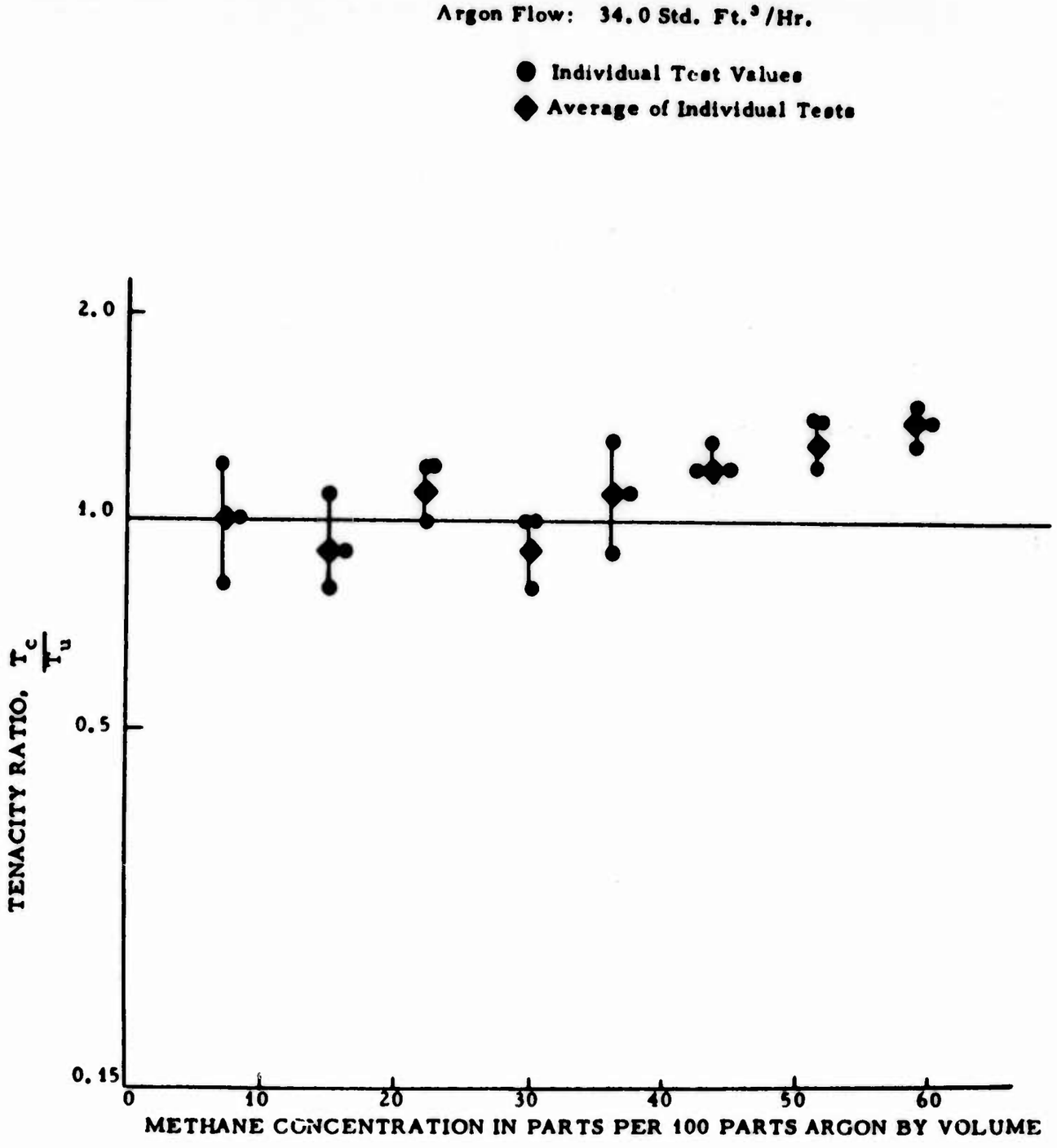


Figure 25. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2100°C, Series 2. Yarn Speed of 25 Ft./Min.

L-1003

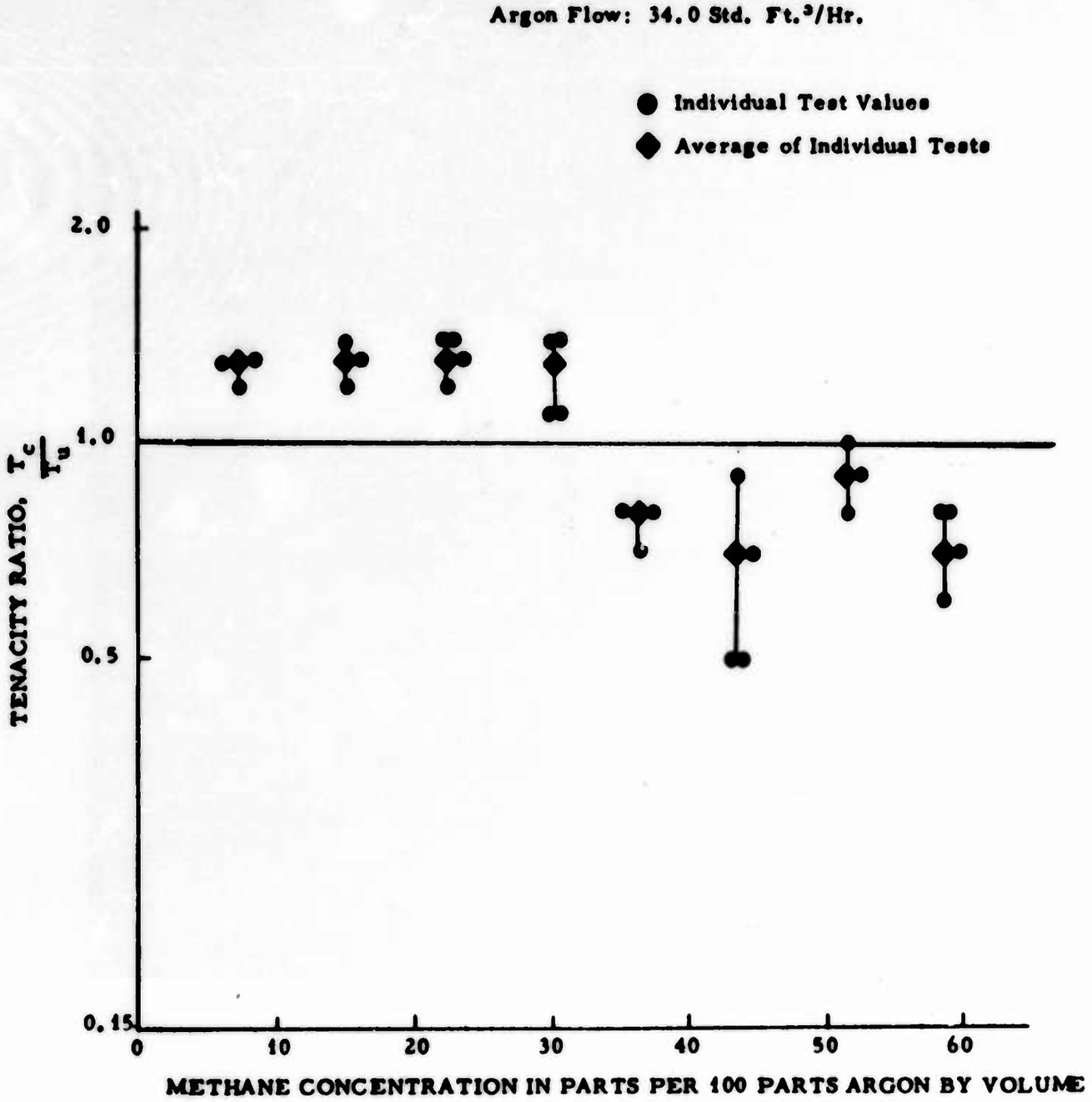


Figure 26. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2200°C, Series 2: Yarn Speed of 25 Ft./Min.

L-1004

Table 16. Data for Figure 22

Yarn Lot No.	UNCOATED YARN	507193-1
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
550	7.4	36.2	3	1720	4.3	1.1	1.0
551	14.6	38.3	3	1710	4.5	1.2	1.1
552	21.9	41.3	3	1740	4.7	1.2	1.1
553	29.2	44.7	3	1760	4.4	1.1	1.0
554	36.5	46.2	3	1760	3.0	0.8	0.7
555	43.6	48.8	3	1770	4.2	1.1	1.0
556	51.2	51.1	3	1770	4.4	1.1	1.0
557	58.8	53.6	3	1780	3.5	0.9	0.8

Table 17. Data for Figure 23

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
558	7.4	36.2	4	1740	3.8	1.0	0.9
559	14.6	38.3	4	1720	4.2	1.1	1.0
560	21.9	41.3	4	1770	4.4	1.1	1.0
561	29.2	44.7	3	1790	4.7	1.2	1.1
562	36.5	46.2	3	1690	3.4	0.9	0.8
563	43.6	48.8	3	1690	4.6	1.3	1.2
564	51.2	51.1	3	1890	5.6	1.3	1.2
565	58.8	53.6	3	1760	5.1	1.3	1.2

Table 18. Data for Figure 24

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
566	7.4	36.2	4	1690	4.5	1.2	1.1
567	14.6	38.3	3	1680	3.9	1.1	1.0
568	21.9	41.3	3	1670	3.9	1.1	1.0
569	29.2	44.7	4	1710	4.0	1.1	1.0
570	36.5	46.2	3	1750	4.9	1.3	1.2
571	43.6	48.8	3	1760	5.0	1.3	1.2
572	51.2	51.1	3	1850	5.7	1.4	1.3
573	58.8	53.6	3	1820	4.7	1.2	1.1

Table 19. Data for Figure 25

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
574	7.4	36.2	3	1450	3.4	1.1	1.0
575	14.6	38.3	3	1670	3.7	1.0	0.9
576	21.9	41.3	3	1700	4.6	1.2	1.1
577	29.2	44.7	3	1740	3.9	1.0	0.9
578	36.5	46.2	3	1760	4.8	1.2	1.1
579	43.6	48.8	3	1800	5.3	1.3	1.2
580	51.2	51.1	3	1840	5.8	1.4	1.3
581	58.8	53.6	3	1910	6.3	1.5	1.4

Table 20. Data for Figure 26

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 25 Ft. /Min.

Expt. No.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
582	7.4	36.2	3	1650	4.9	1.4	1.3
583	14.6	38.3	4	1760	5.3	1.4	1.3
584	21.9	41.3	4	1840	5.6	1.4	1.3
585	29.2	44.7	4	1700	5.1	1.4	1.3
586	36.5	46.2	3	1790	3.6	0.9	0.8
587	43.6	48.8	4	1860	3.0	0.8	0.7
588	51.2	51.1	3	1850	4.0	1.0	0.9
589	58.8	53.6	4	1810	3.1	0.8	0.7

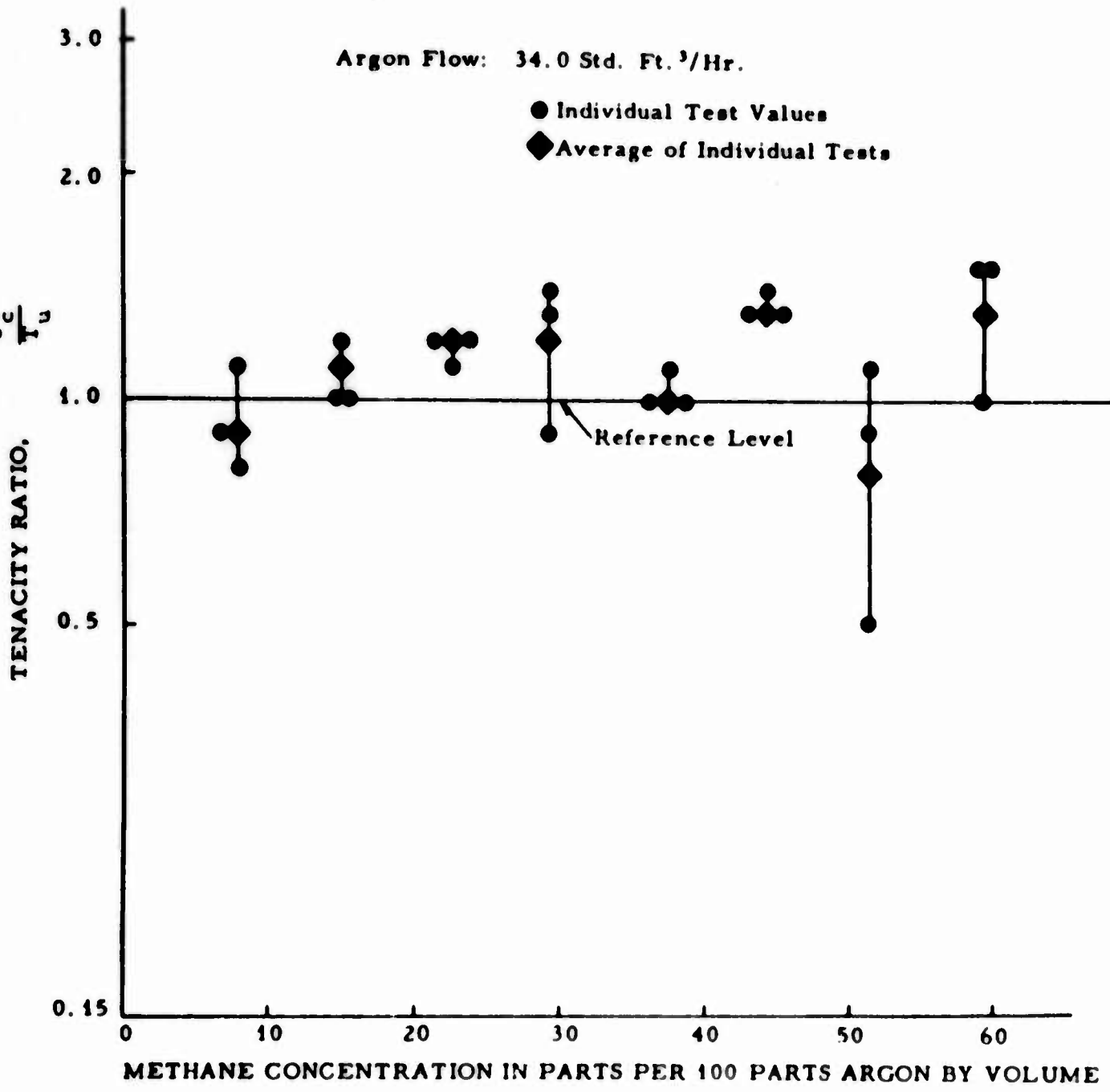


Figure 27. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1800°C, Series 2: Yarn Speed of 21 Ft./Min.

L-1005

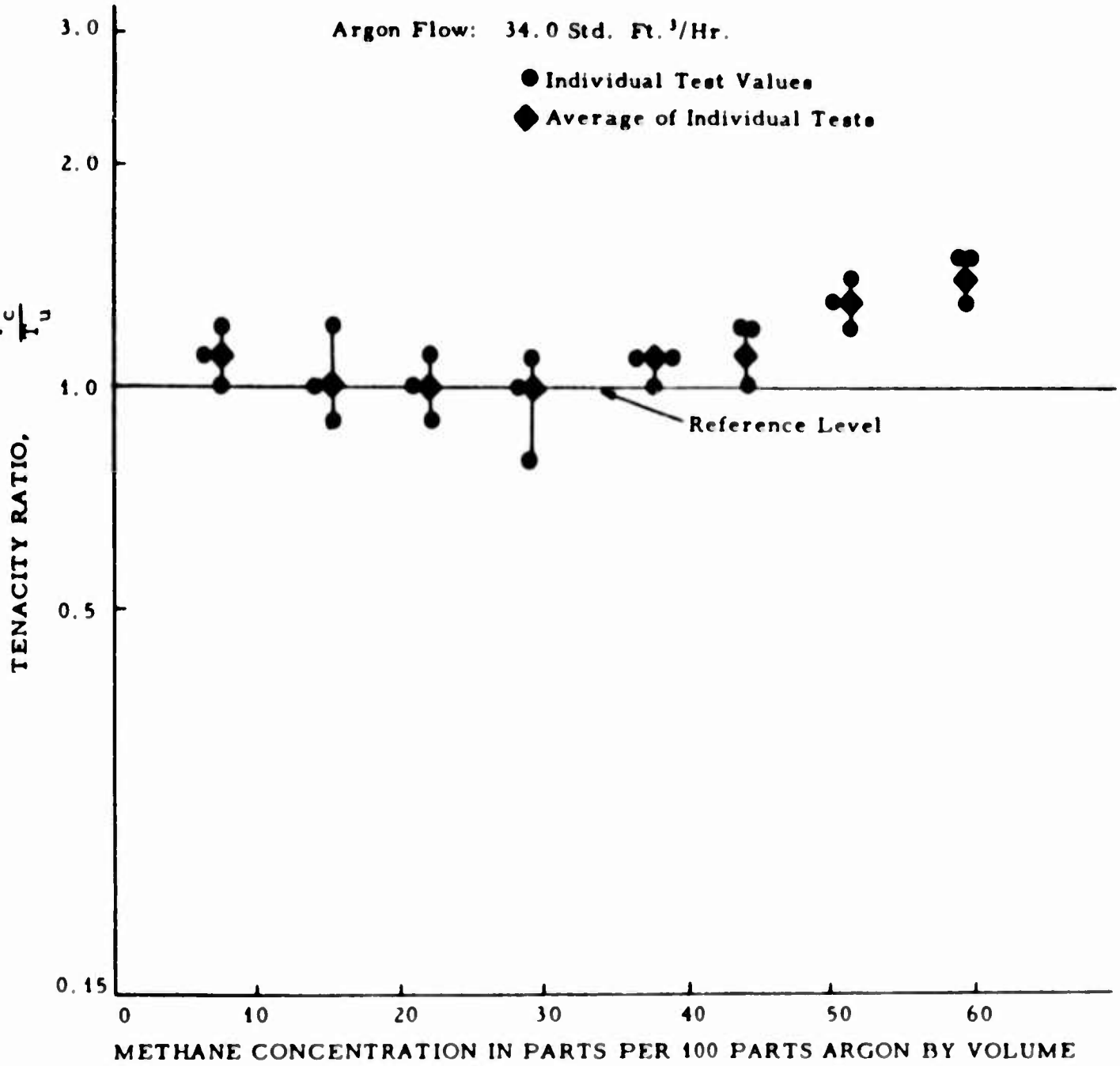


Figure 28. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1900°C, Series 2: Yarn Speed of 21 Ft./Min.

L-1006

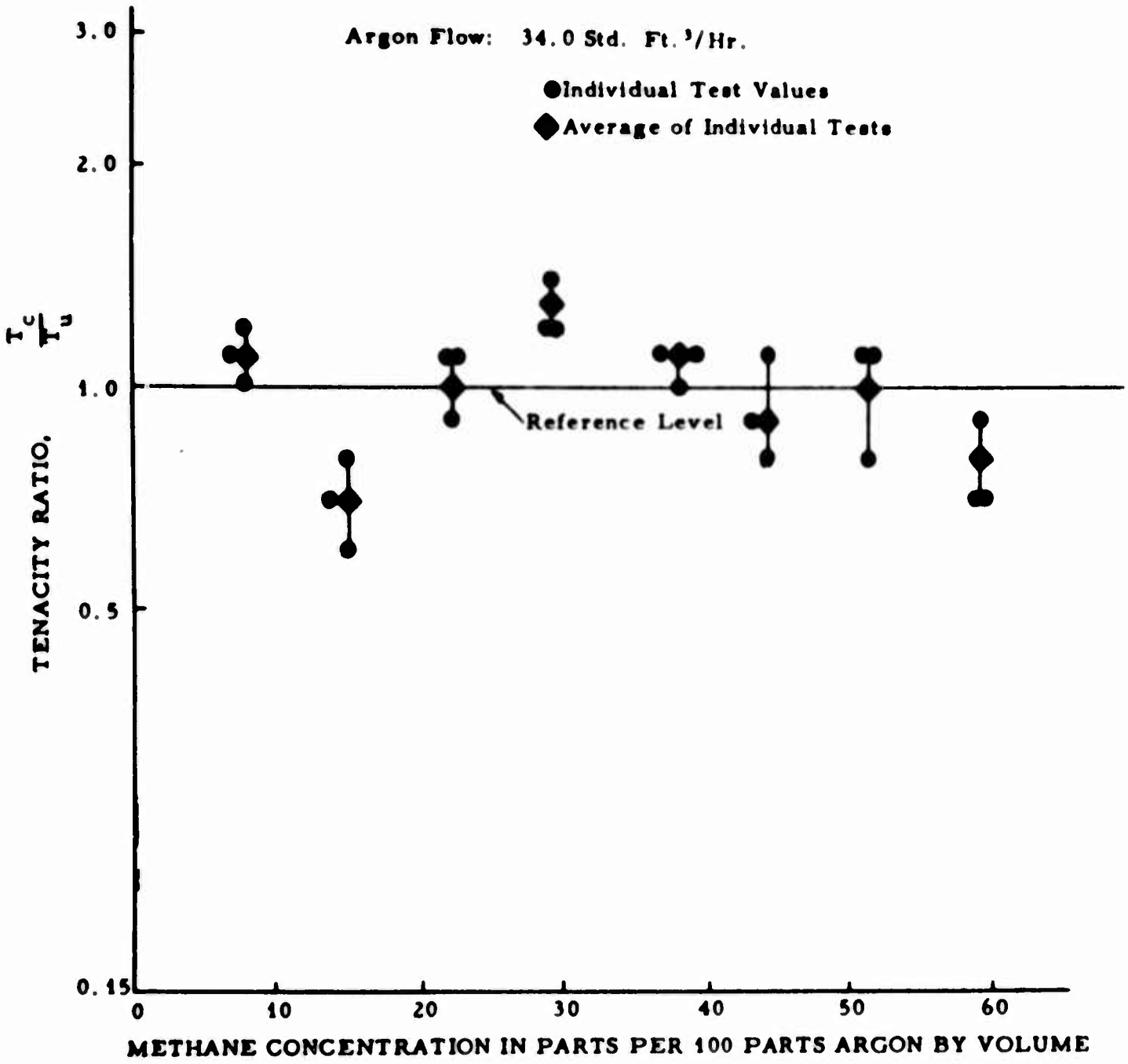


Figure 29. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2000°C, Series 2: Yarn Speed of 21 Ft./Min.

L-1007

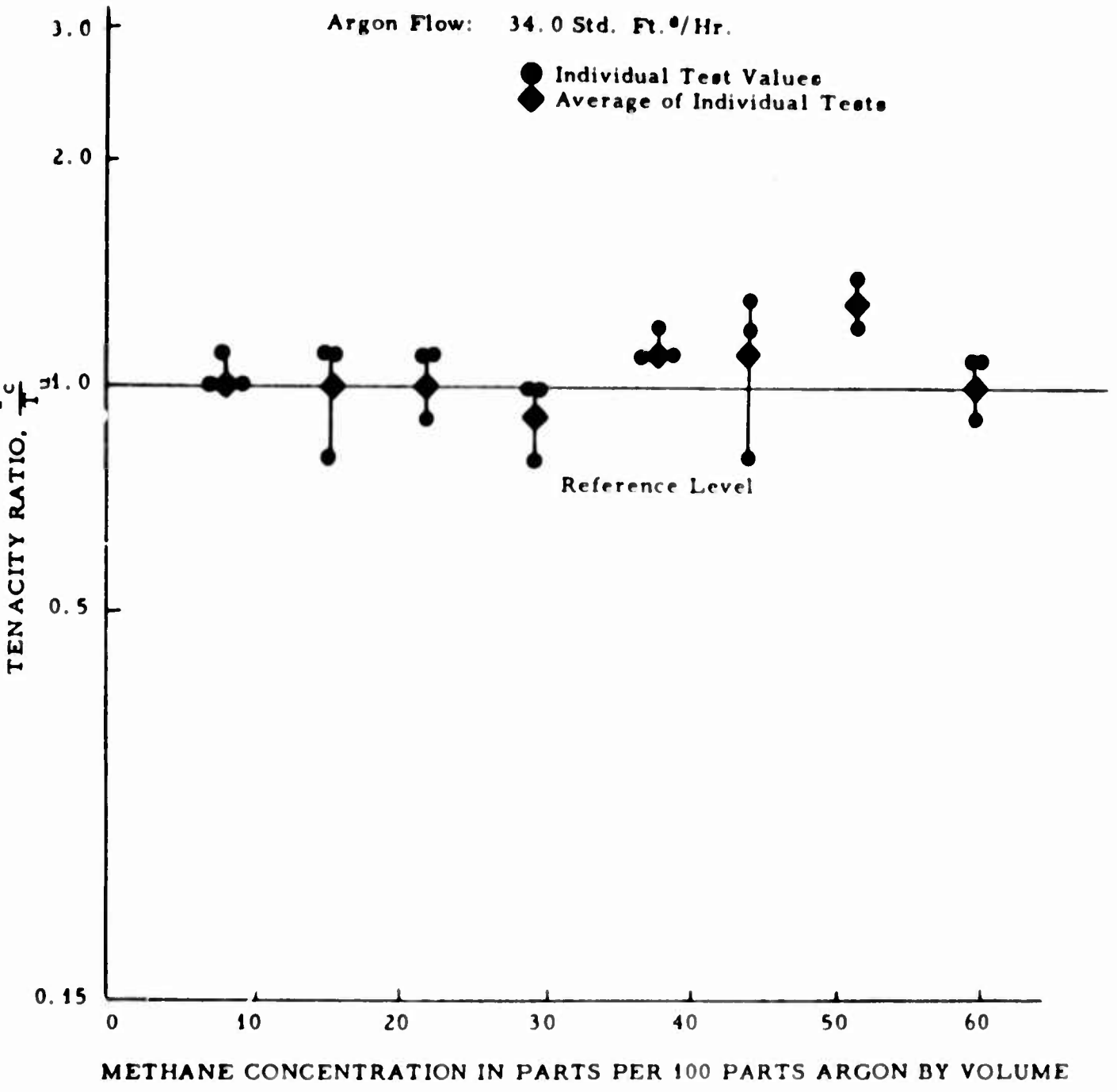


Figure 30. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2100°C, Series 2: Yarn Speed of 21 Ft./Min.

L-1008

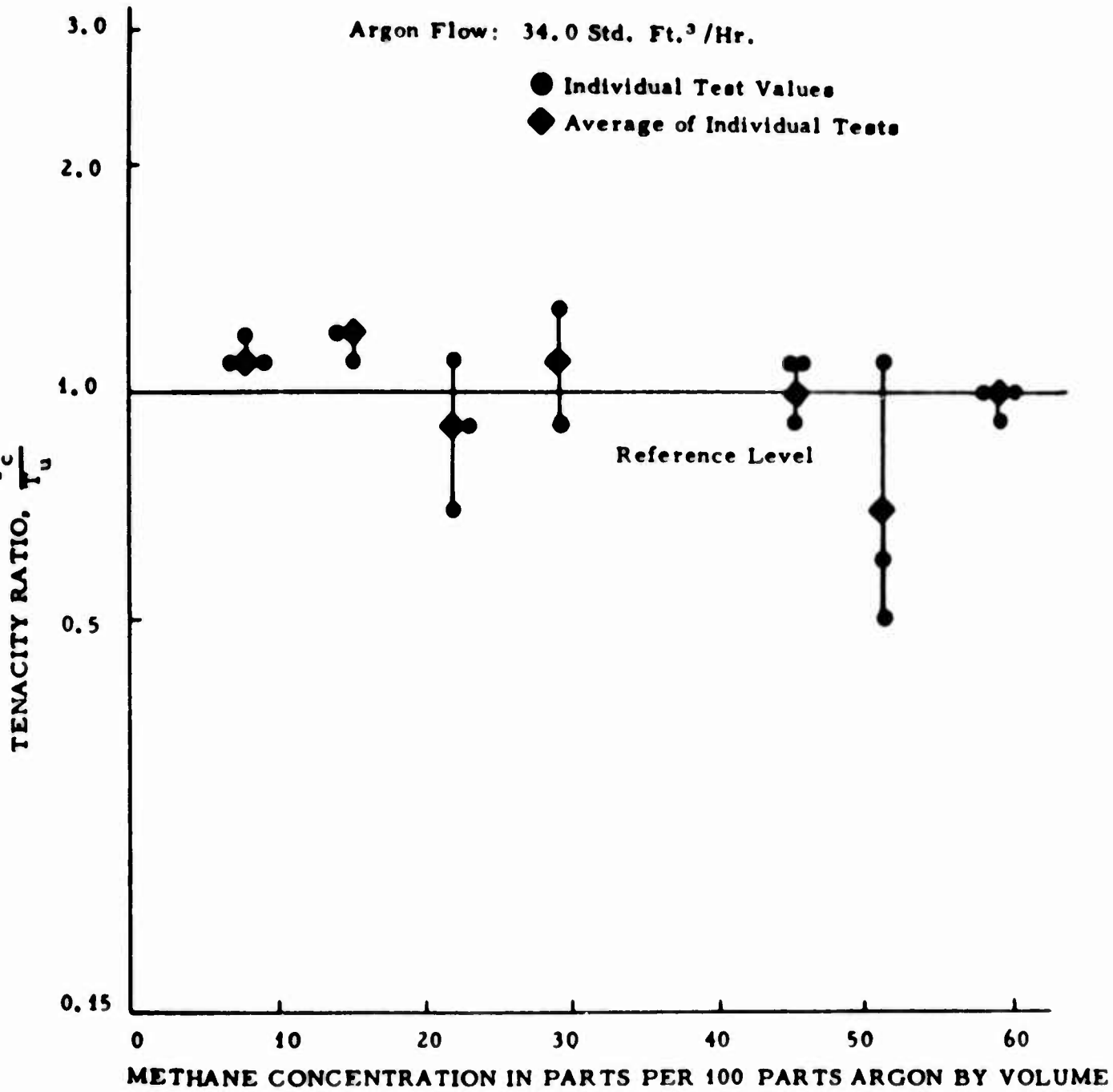


Figure 31. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2200°C, Series 2: Yarn Speed of 21 Ft./Min. L-1009

Table 21. Data for Figure 27

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 21 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
590	7.4	36.2	3	1620	3.7	1.0	0.9
591	14.6	38.3	3	1660	4.3	1.2	1.1
592	21.9	41.3	3	1660	4.6	1.3	1.2
593	29.2	44.7	3	1760	5.0	1.3	1.2
594	36.5	46.2	3	1770	4.4	1.1	1.0
595	43.7	48.6	3	1820	5.9	1.5	1.3
596	51.2	51.1	3	1700	3.5	0.9	0.8
597	58.8	53.6	3	1760	5.4	1.4	1.3

Table 22. Data for Figure 28

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 21 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
598	7.4	36.2	3	1690	4.4	1.2	1.1
599	14.6	38.3	3	1670	4.2	1.1	1.0
600	21.9	41.3	3	1750	4.3	1.1	1.0
601	29.2	44.7	3	1800	4.3	1.1	1.0
602	36.5	46.2	3	1760	4.5	1.2	1.1
603	43.7	48.6	3	1800	4.9	1.2	1.1
604	51.2	51.1	3	1890	5.7	1.4	1.3
605	58.8	53.6	3	1940	6.6	1.5	1.4

Table 23. Data for Figure 29

UNCOATED YARN

Yarn Lot No.	5071
Average Pull Strength, Heat-Treated Form, lbs.:	4.0
Average Denier, Heat Treated Form, g/9000 M:	1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:	1.1

COATED YARN

Yarn Speed: 21 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
606	7.4	36.2	3	1690	4.6	1.2	1.1
607	14.6	38.3	3	1680	3.0	0.8	0.7
608	21.9	41.3	3	1760	4.4	1.1	1.0
609	29.2	44.7	3	1830	5.5	1.4	1.3
610	36.5	46.2	3	1790	4.6	1.2	1.1
611	43.7	48.6	3	1790	4.1	1.0	0.9
612	51.2	51.1	3	1815	4.4	1.1	1.0
613	58.8	53.6	3	1870	3.6	0.9	0.8

Table 24. Data for Figure 30

UNCOATED YARN

Yarn Lot No.	5071
Average Pull Strength, Heat-Treated Form, lbs.:	4.0
Average Denier, Heat Treated Form, g/9000 M:	1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:	1.1

COATED YARN

Yarn Speed: 21 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Average Tenacity Ratio
614	7.4	36.2	3	1760	4.4	1.1	1.0
615	14.6	38.3	3	1830	4.4	1.1	1.0
616	21.9	41.3	3	1870	4.6	1.1	1.0
617	29.2	44.7	3	1900	4.4	1.0	0.9
618	36.5	46.2	3	1920	5.1	1.2	1.1
619	43.7	48.8	3	1760	4.6	1.2	1.1
620	51.2	51.1	3	1860	5.7	1.4	1.3
621	58.8	53.6	3	1760	4.3	1.1	1.0

Table 25. Data for Figure 31

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat Treated Form, g/9000 M:		1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.1

COATED YARN

Yarn Speed: 21 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
622	7.4	36.2	3	1630	3.1	1.2	1.1
623	14.6	38.3	2	1730	4.8	1.3	1.2
624	21.9	41.3	3	1730	3.7	1.0	0.9
625	29.2	44.7	2	1810	5.0	1.2	1.1
626	36.5	46.2	*	*	*	*	*
627	43.7	48.8	3	1790	4.5	1.1	1.0
628	51.2	51.1	3	1790	3.0	0.8	0.7
629	58.8	53.6	3	1750	4.3	1.1	1.0

* Information not available

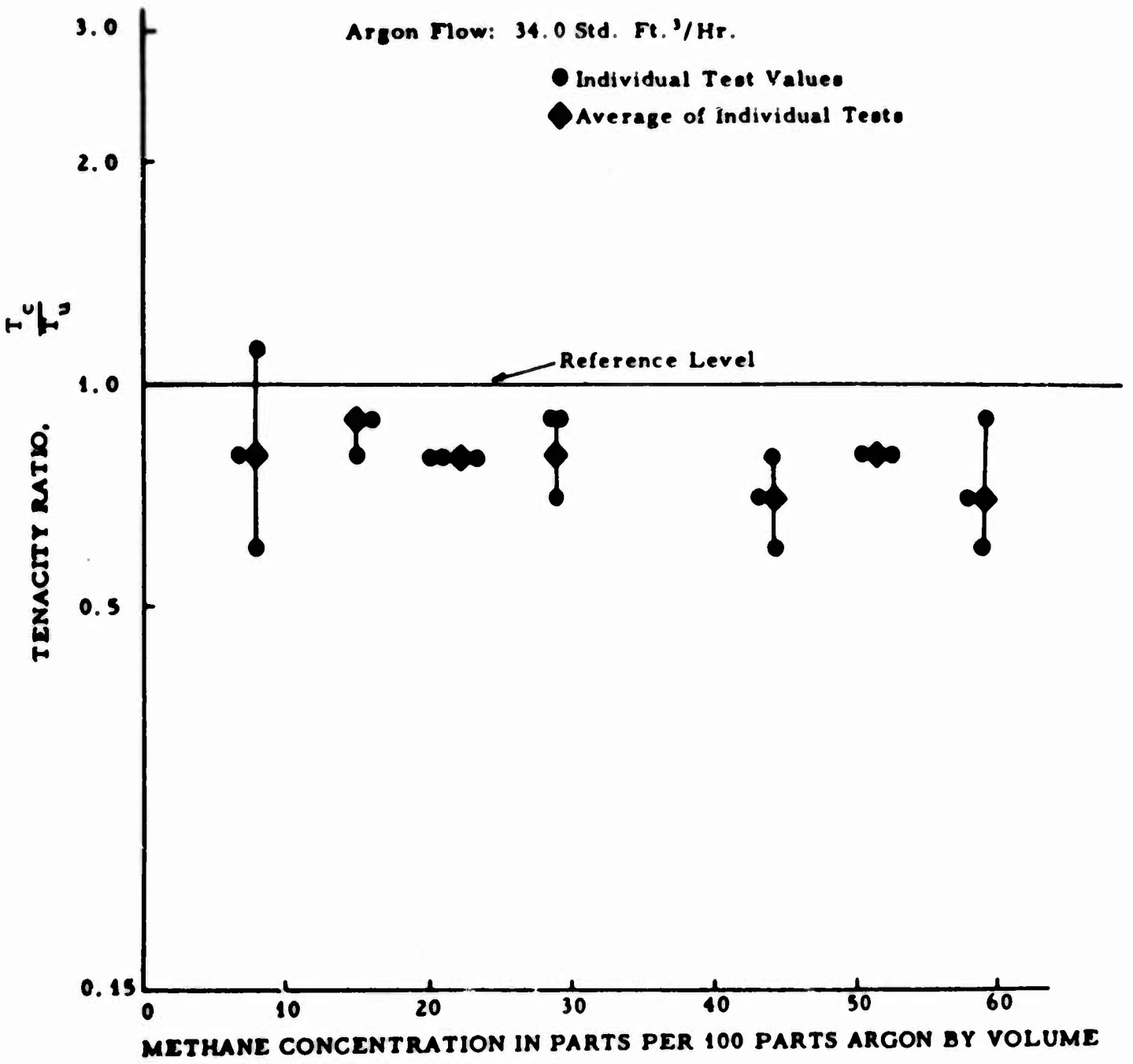


Figure 32. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1800°C, Series 3: Yarn Speed of 17 Ft./Min.

L-1010

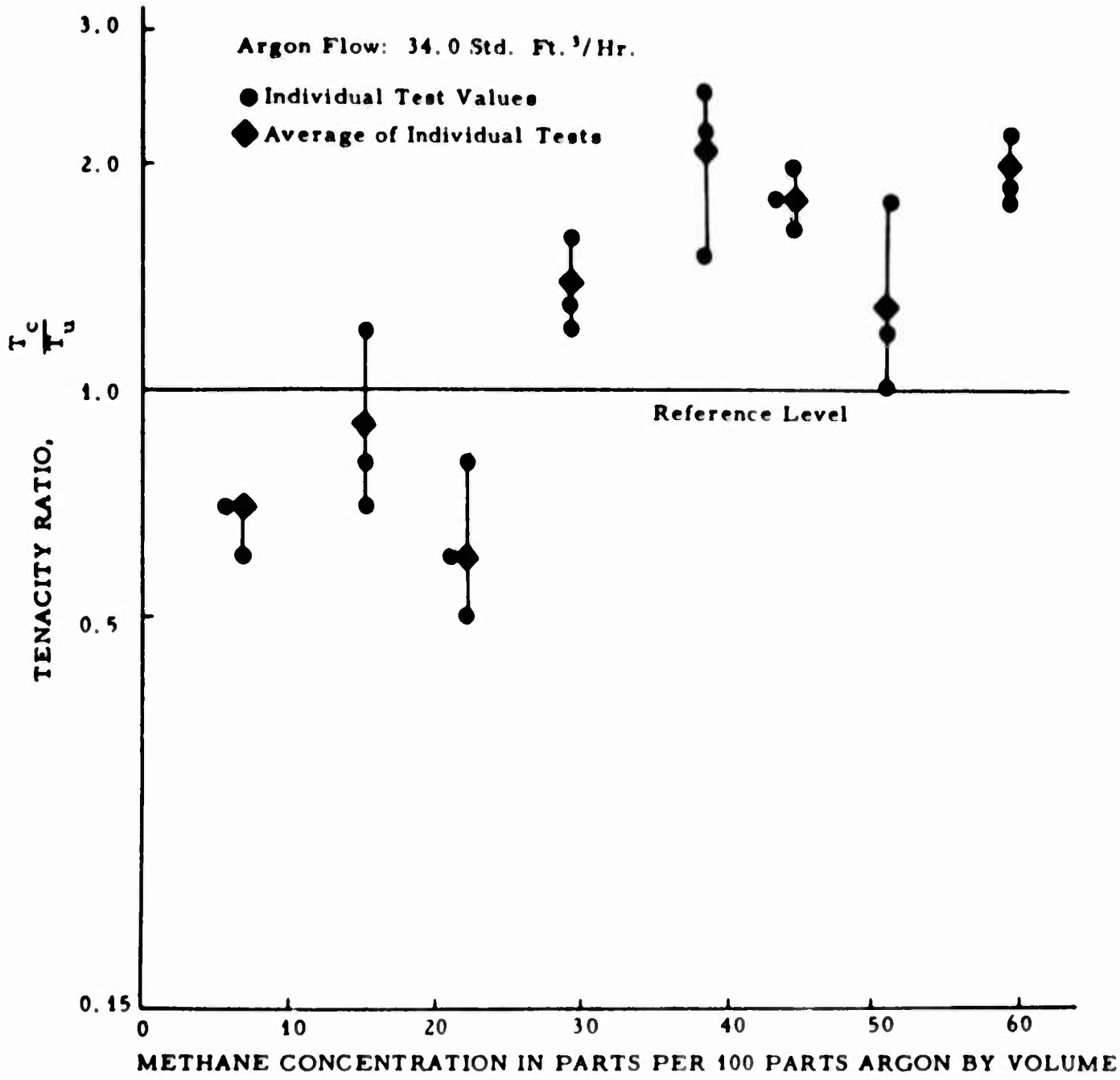


Figure 33. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1900°C, Series 3: Yarn Speed of 17 Ft./Min.

L-1011

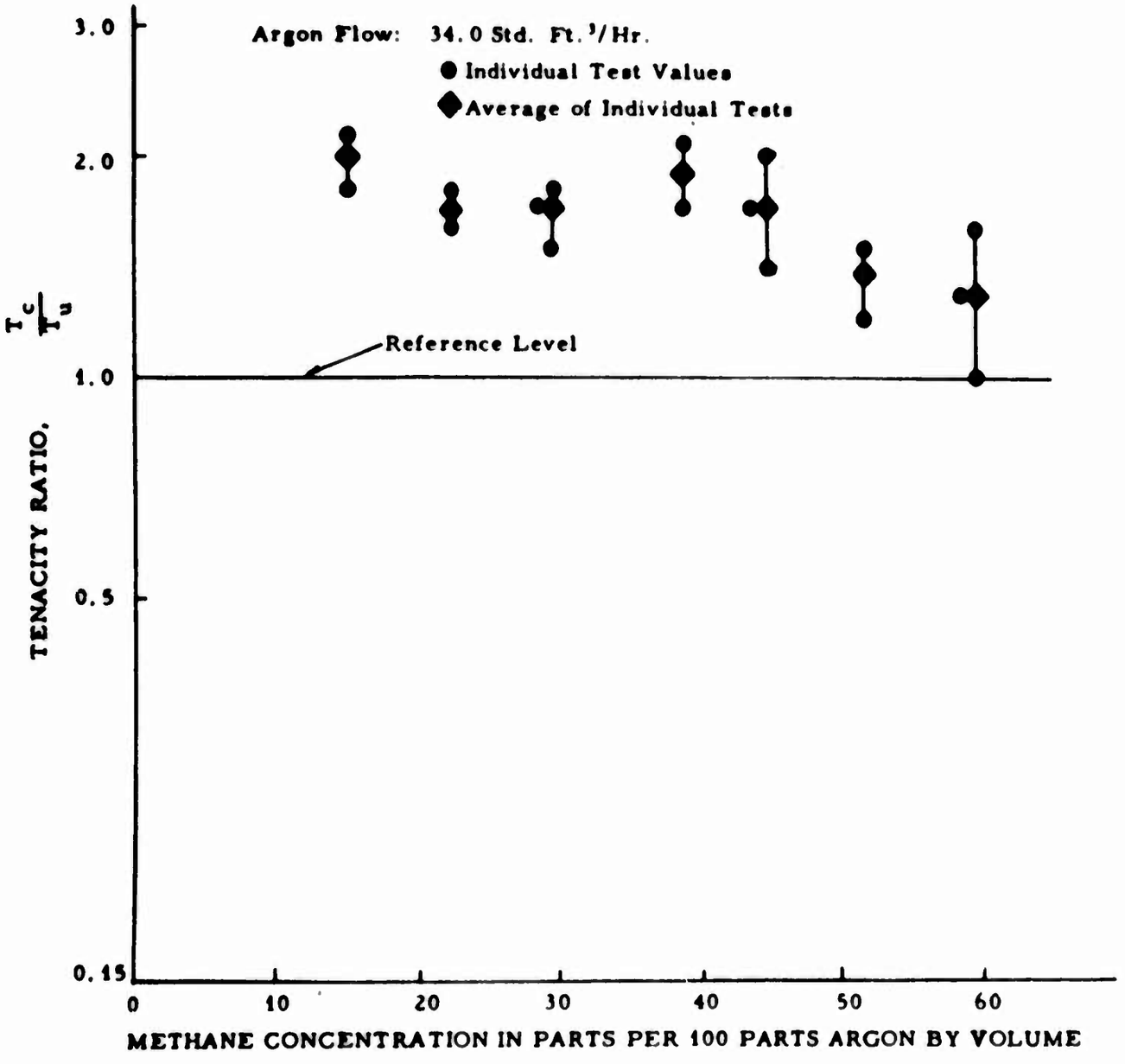


Figure 34. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2000°C, Series 3: Yarn Speed of 17 Ft./Min.

L-1012

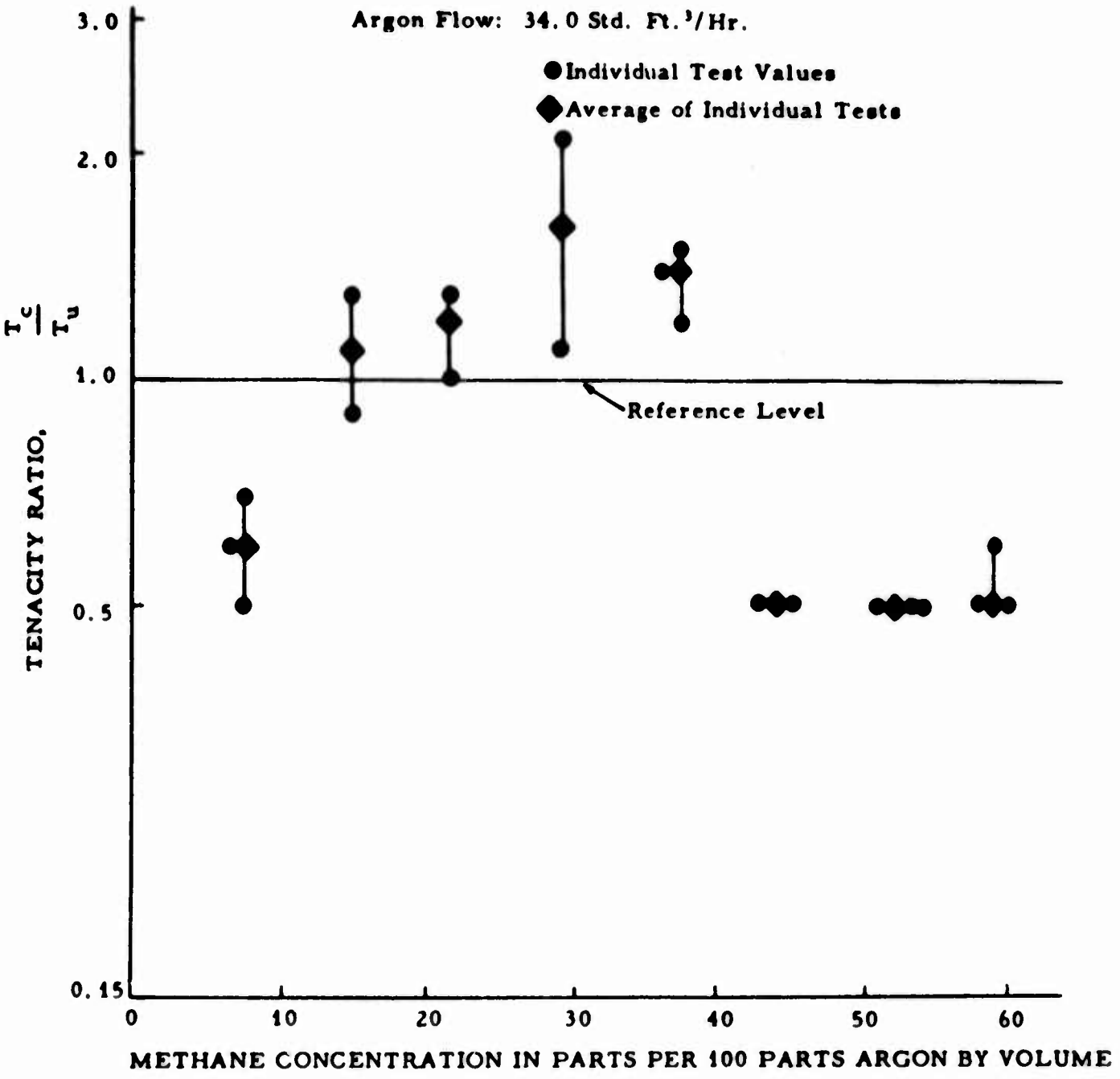


Figure 35. Tenacity Ratio of Yarn Coated in Chamber B at a Deposition Temperature of 2100°C, Series 3: Yarn Speed of 17 Ft./Min.

L-1013

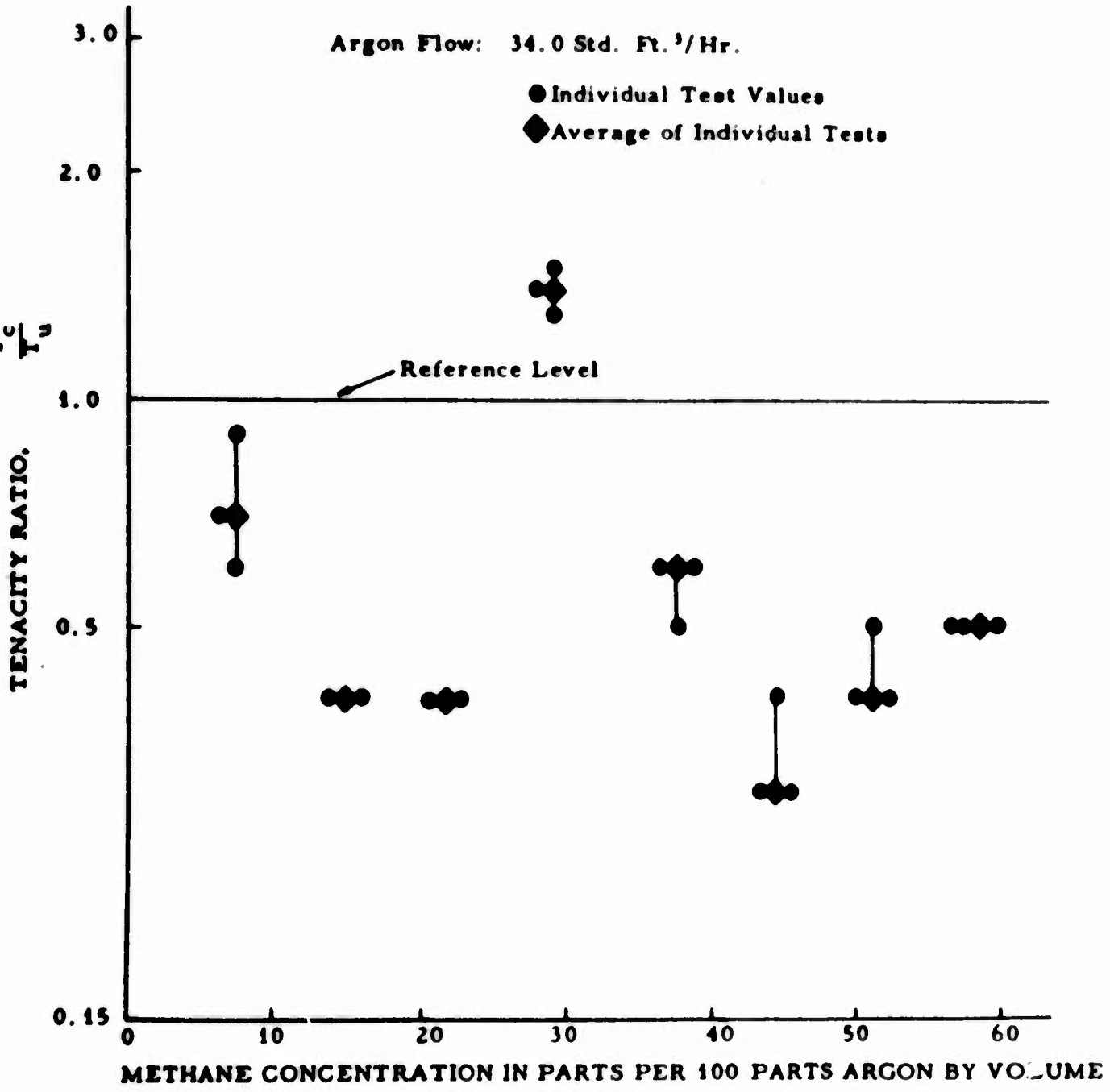


Figure 36. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2200°C, Series 3: Yarn Speed of 17 Ft./Min.

L-1014

Table 26. Data for Figure 32

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat Treated Form, g/9000 M:		1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.1

COATED YARN

Yarn Speed: 17 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
630	7.4	36.2	3	1590	3.1	0.9	0.8
631	14.6	38.3	2	1590	3.4	1.0	0.9
632	21.9	41.3	3	1530	3.1	0.9	0.8
633	29.2	44.7	3	1680	3.4	0.9	0.8
634	36.5	46.2	*	*	*	*	*
635	43.7	48.8	3	1640	2.9	0.8	0.7
636	51.2	51.1	2	1590	3.0	0.9	0.8
637	58.8	53.6	3	1670	3.1	0.8	0.7

*Information not available

Table 27. Data for Figure 33

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat Treated Form, g/900 M:		1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.1

COATED YARN

Yarn Speed: 17 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std.Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
638	7.4	36.2	2	1520	2.6	0.8	0.7
639	14.6	38.3	3	1700	3.6	1.0	0.9
640	21.9	41.3	3	1790	2.9	0.7	0.6
641	29.2	44.7	3	1870	6.2	1.5	1.4
642	36.5	46.2	3	1820	8.7	2.2	2.1
643	43.6	48.8	3	1910	8.0	1.9	1.8
644	51.2	51.1	3	1870	5.7	1.4	1.3
645	58.8	53.6	3	1890	8.8	2.1	2.0

Table 28. Data for Figure 34

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat Treated Form, g/9000 M:		1680 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.1

COATED YARN

Yarn Speed: 17 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. Ft^3/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
646	7.4	36.2					
647	14.6	38.3	2	1770	8.2	2.1	2.0
648	21.9	41.3	2	1800	7.1	1.8	1.7
649	29.2	44.7	3	1850	7.3	1.8	1.7
650	36.5	46.2	2	1875	8.2	2.0	1.9
651	43.6	48.8	3	1770	7.0	1.8	1.7
652	51.2	51.1	2	1800	5.9	1.5	1.4
653	58.8	53.6	3	1760	5.4	1.4	1.3

Table 29. Data for Figure 35

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 17 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3$/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
654	7.4	36.2	3	1590	2.4	0.7	0.6
655	14.6	38.3	2	1640	4.3	1.2	1.1
656	21.9	41.3	2	1650	4.7	1.3	1.2
657	29.2	44.7	2	1740	6.5	1.7	1.6
658	36.5	46.2	3	1870	6.2	1.5	1.4
659	43.6	48.8	2	1810	2.4	0.6	0.5
660	51.2	51.1	3	1910	2.5	0.6	0.5
661	58.8	53.6	3	1960	2.6	0.6	0.5

Table 30. Data for Figure 36

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 17 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std.Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
662	7.4	36.2	3	1640	3.0	0.8	0.7
663	14.6	38.3	2	1770	1.3	0.5	0.4
664	21.9	41.3	2	1850	1.4	0.5	0.4
665	29.2	44.7	3	1680	5.5	1.5	1.4
666	36.5	46.2	3	1700	2.5	0.7	0.6
667	43.6	48.8	3	1820	1.5	0.4	0.3
668	51.2	51.1	3	1900	1.9	0.5	0.4
669	58.8	53.6	3	1940	2.4	0.6	0.5

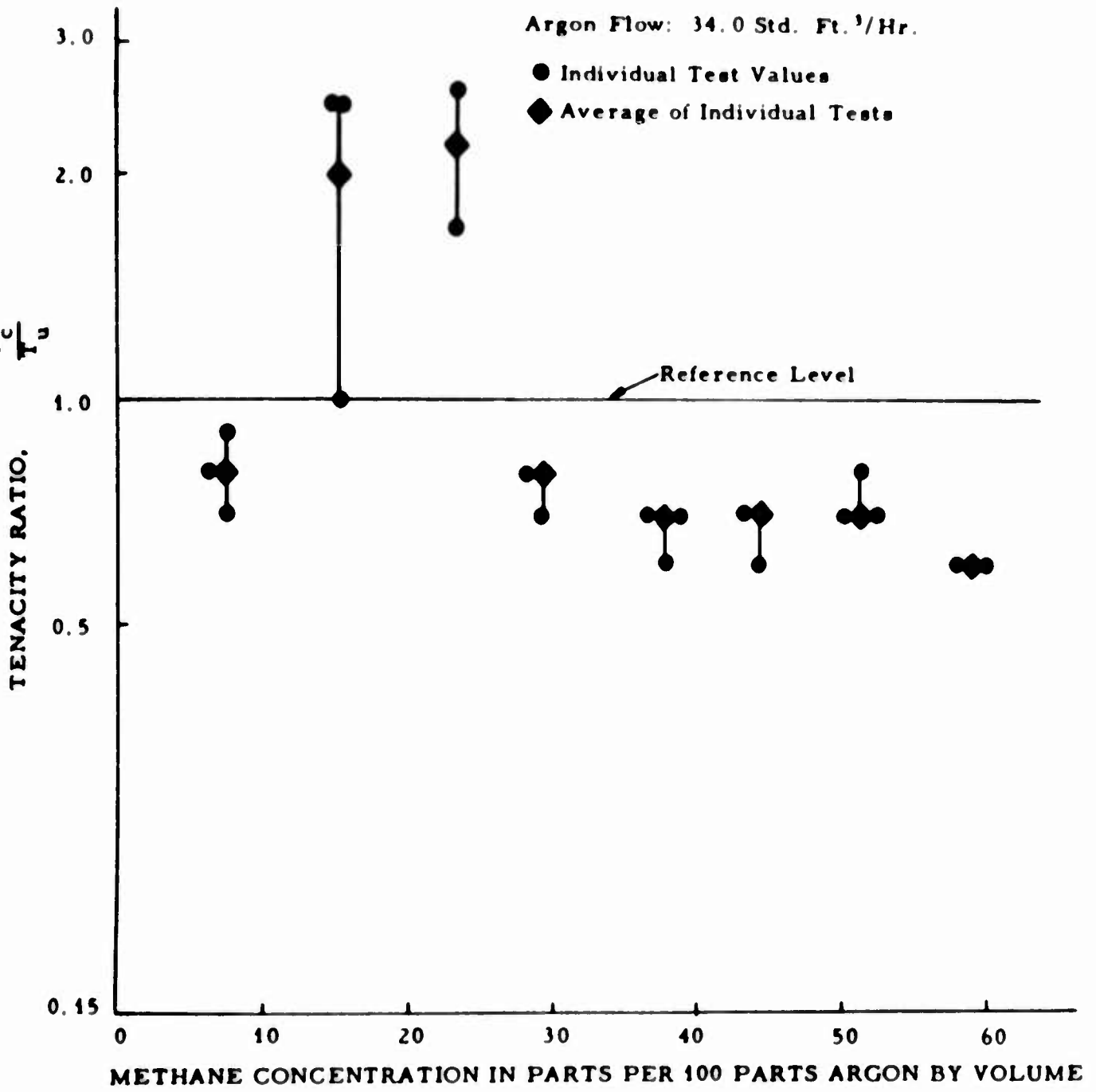


Figure 37. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1800°C, Series 4: Yarn Speed of 13 Ft./Min.

L-1015

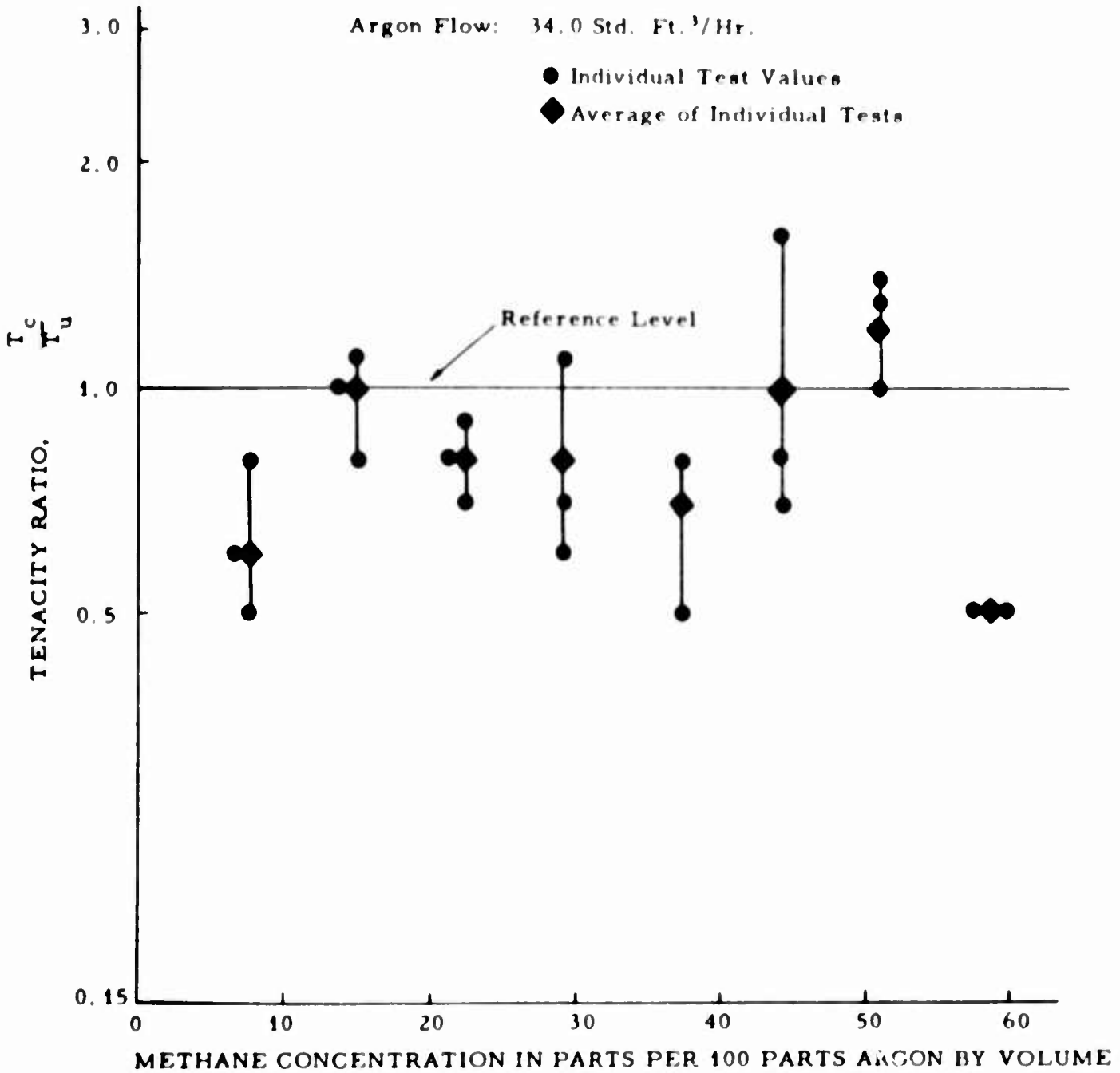


Figure 38. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 1900°C, Series 4: Yarn Speed of 13 Ft./Min.

L-1016

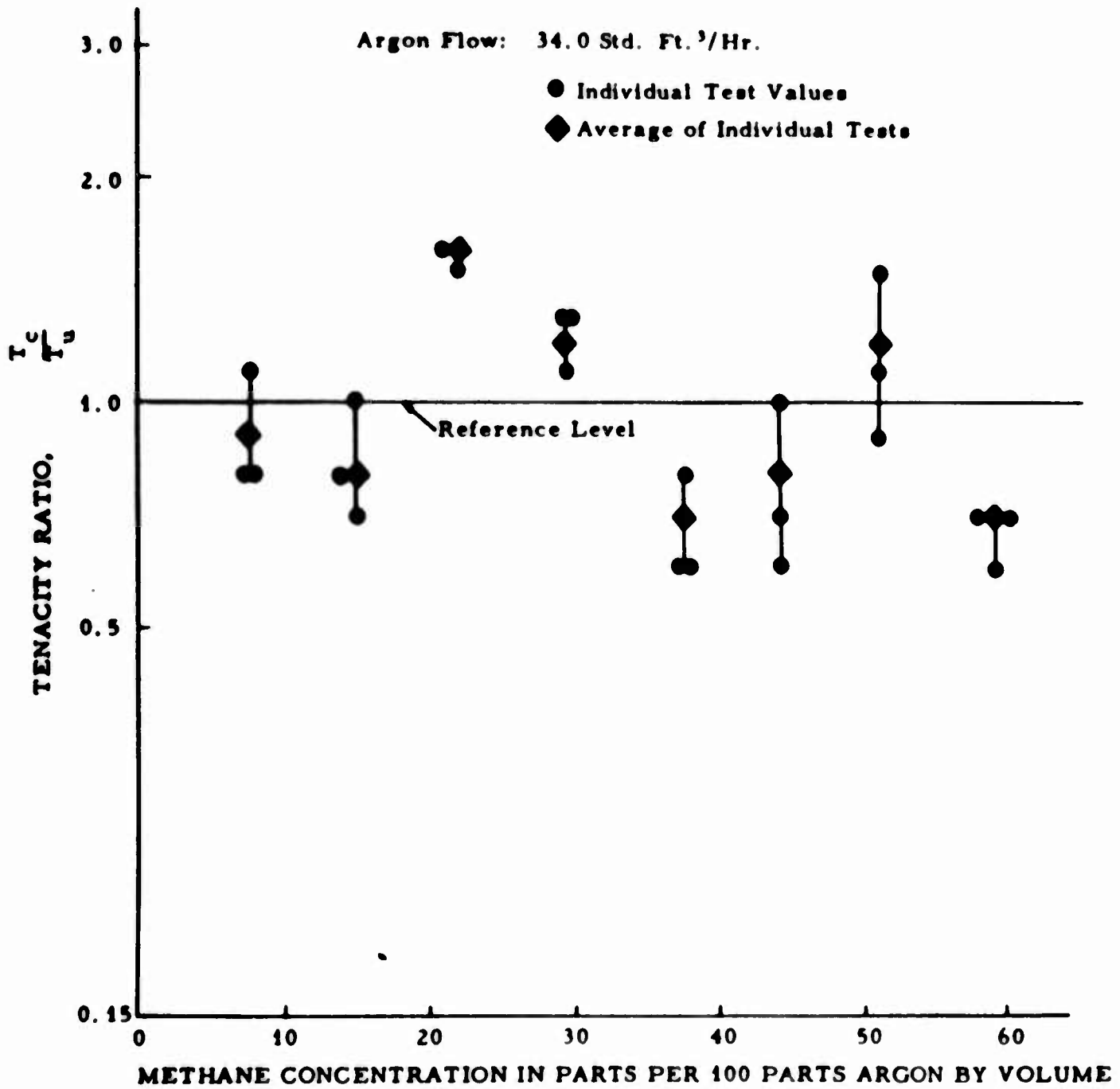


Figure 39. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2000°C, Series 4: Yarn Speed of 13 Ft./Min.

L-1017

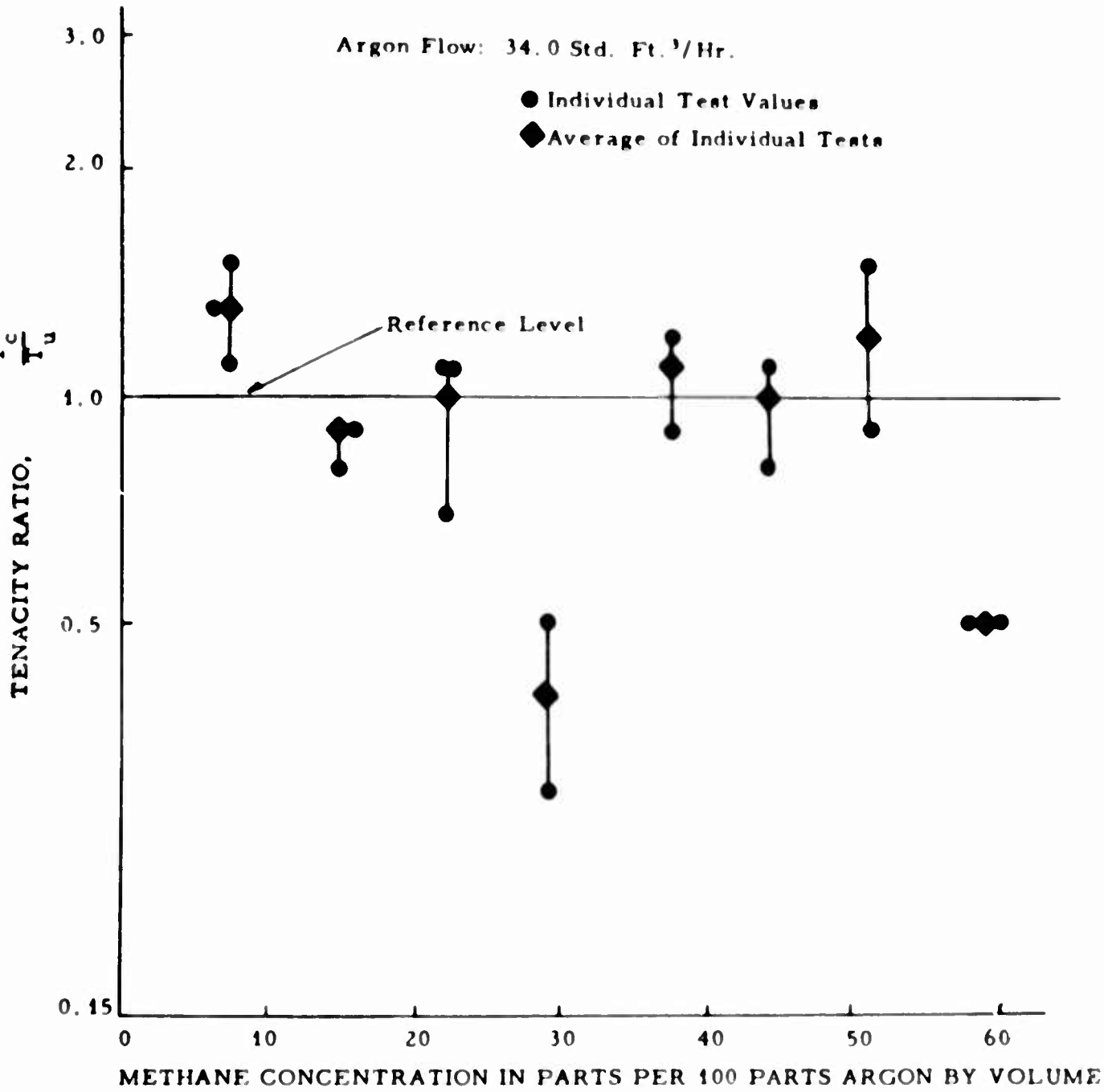


Figure 40. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2100°C, Series 4: Yarn Speed of 13 Ft./Min.

L-1018

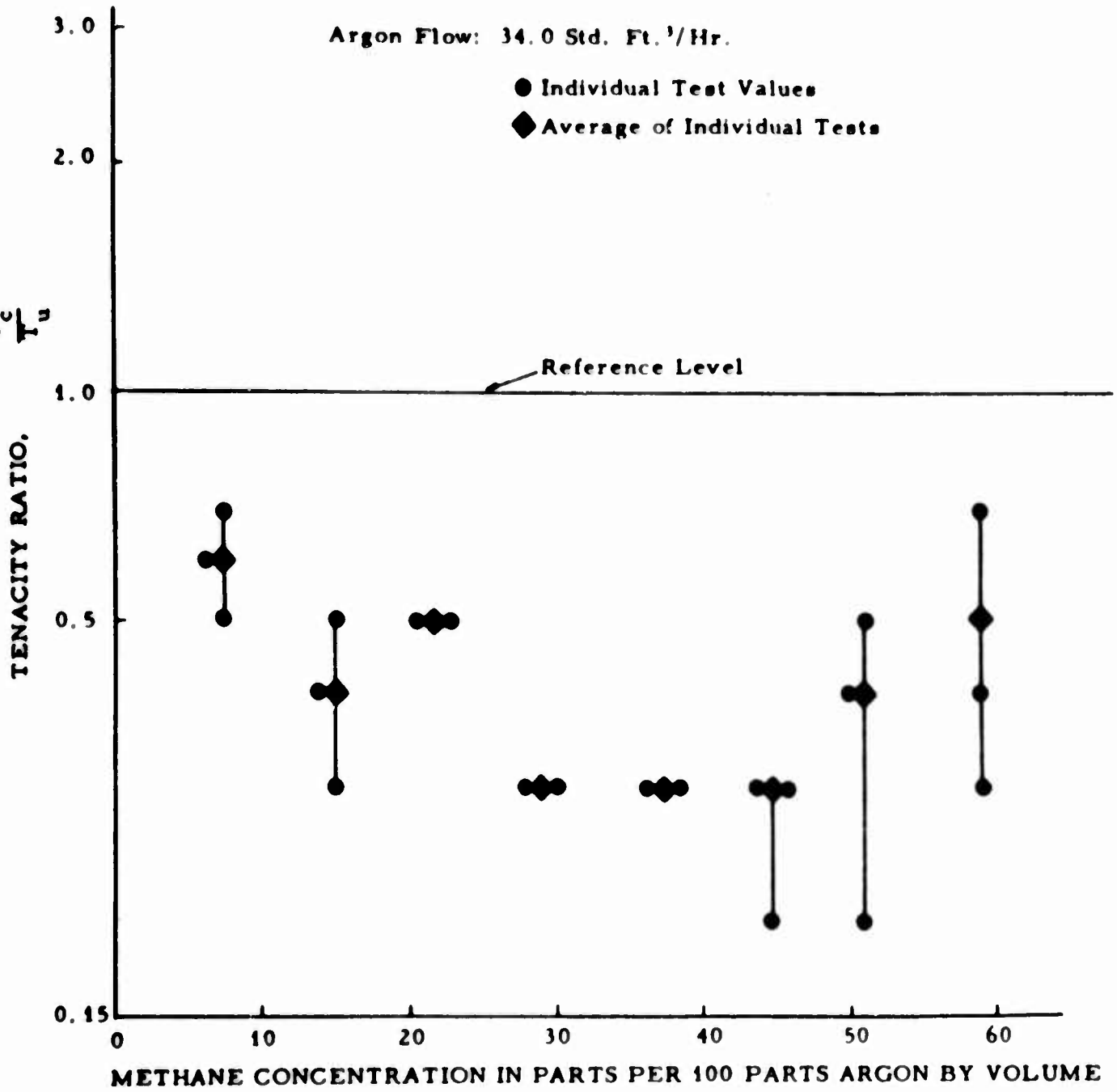


Figure 41. Tenacity Ratio of Yarn Coated in Chamber C at a Deposition Temperature of 2200°C, Series 4: Yarn Speed of 13 Ft./Min.

L-1019

Table 31. Data for Figure 37

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 13 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
670	7.4	36.2	3	1460	2.9	0.9	0.8
671	14.6	38.3	3	1520	7.0	2.1	2.0
672	21.9	41.3	2	1760	8.8	2.3	2.2
673	29.2	44.7	2	1590	3.0	0.9	0.8
674	36.5	46.2	3	1560	2.6	0.8	0.7
675	43.6	48.8	2	1560	2.6	0.8	0.7
676	51.2	51.1	3	1700	3.1	0.8	0.7
677	58.8	53.6	2	1660	2.4	0.7	0.6

Table 32. Data for Figure 38

Yarn Lot No.	UNCOATED YARN	5071
Average Pull Strength, Heat-Treated Form, lbs.:		4.0
Average Denier, Heat-Treated Form, g/9000 m:		1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:		1.1

COATED YARN

Yarn Speed: 13 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
678	7.4	36.2	3	1480	2.3	0.7	0.6
679	14.6	38.3	3	1710	4.0	1.1	1.0
680	21.9	41.3	3	1810	3.8	0.9	0.8
681	29.2	44.7	3	1750	3.6	0.9	0.8
682	36.5	46.2	3	1650	3.0	0.8	0.7
683	43.6	48.8	3	1560	3.7	1.1	1.0
684	51.2	51.1	3	1780	5.0	1.3	1.2
685	58.8	53.6	2	1790	2.5	0.6	0.5

Table 33. Data for Figure 39

UNCOATED YARN

Yarn Lot No.	5071
Average Pull Strength, Heat-Treated Form, lbs.:	4.0
Average Denier, Heat-Treated Form, g/9000 m:	1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:	1.1

COATED YARN

Yarn Speed: 13 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std.Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
686	7.4	36.2	3	1640	3.6	1.0	0.9
687	14.6	38.3	3	1750	3.5	0.9	0.8
688	21.9	41.3	2	1850	6.8	1.7	1.6
689	29.2	44.7	3	1910	5.5	1.3	1.2
690	36.5	46.2	3	1700	3.0	0.8	0.7
691	43.6	48.8	3	1690	3.3	0.9	0.8
692	51.2	51.1	3	1720	4.9	1.3	1.2
693	58.8	53.6	3	1520	2.7	0.8	0.7

Table 34. Data for Figure 40

UNCOATED YARN

Yarn Lot No.	5071
Average Pull Strength, Heat-Treated Form, lbs.:	4.0
Average Denier, Heat-Treated Form, g/9000 m:	1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:	1.1

COATED YARN

Yarn Speed: 13 Ft./Min.

Expt. No.	Meth. Con., Parts/100 Parts Argon	Total Gas Flow Rate, Std.Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
694	7.4	36.2	3	1550	4.8	1.4	1.3
695	14.6	38.3	2	1740	3.9	1.0	0.9
696	21.9	41.3	3	1710	4.1	1.1	1.0
697	29.2	44.7	2	1750	1.9	0.5	0.4
698	36.5	46.2	2	1840	4.8	1.2	1.1
699	43.6	48.8	2	1860	4.5	1.1	1.0
700	51.2	51.1	2	1820	5.2	1.3	1.2
701	58.8	53.6	2	1730	2.3	0.6	0.5

Table 35. Data for Figure 41

UNCOATED YARN

Yarn Lot No.	5071
Average Pull Strength, Heat-Treated Form, lbs.:	4.0
Average Denier, Heat-Treated Form, g/9000 m:	1680 ± 20
Average Tenacity, Heat-Treated Form, g/denier:	1.1

COATED YARN

Yarn Speed: 13 Ft. /Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std.Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
702	7.4	36.2	3	1820	2.7	0.7	0.6
703	14.6	38.3	2	1730	1.8	0.5	0.4
704	21.9	41.3	3	1720	2.2	0.6	0.5
705	29.2	44.7	2	1770	1.5	0.4	0.3
706	36.5	46.2	2	1810	1.5	0.4	0.3
707	43.6	48.8	3	1790	1.2	0.3	0.3
708	51.2	51.1	3	1820	2.0	0.5	0.4
709	58.8	53.6	3	1820	2.3	0.6	0.5

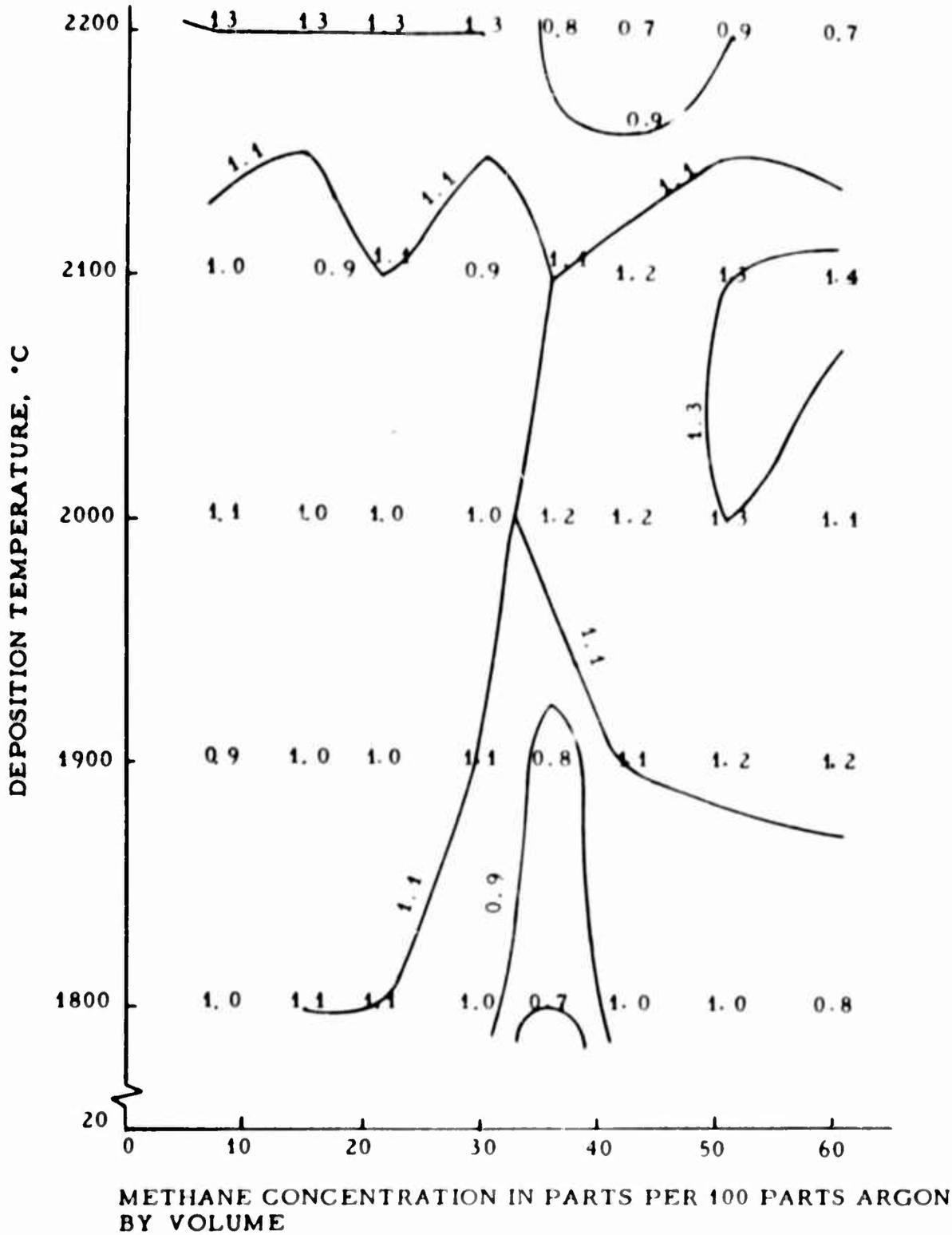


Figure 42. Contour Plot of the Tenacity Ratio as a Function of Methane Concentration and Deposition Temperature, Series 2: Yarn Speed of 25 Ft./Min.

L-1020

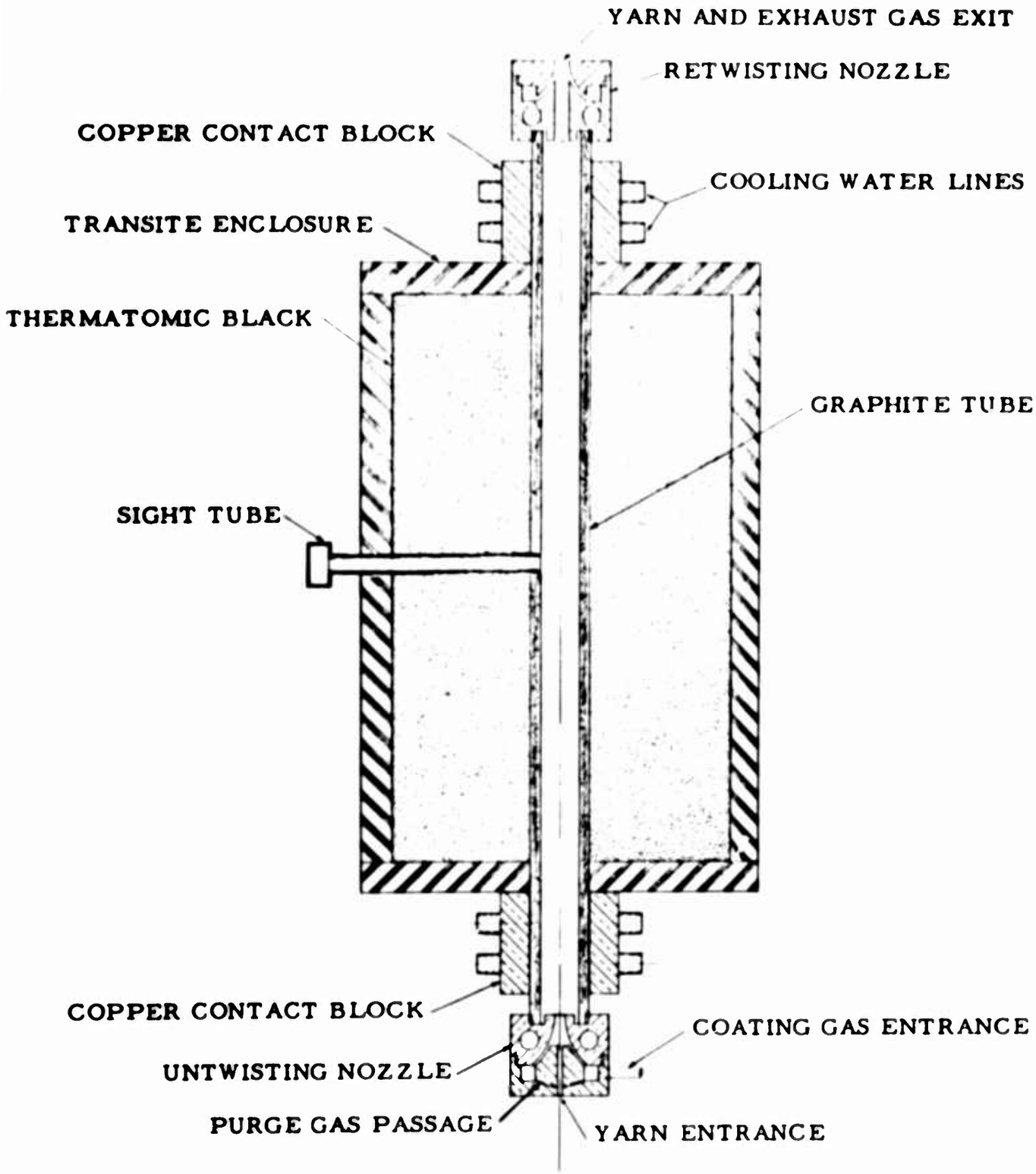
A furnace and coating chamber shown in Figure 43 were designed to prevent both oxidation and arcing. The yarn enters the chamber at room temperature and exits at 200°C which is below the effective oxidation threshold of the yarn. Inside the chamber, the yarn is heated by radiation from a graphite tube heating element. Oxygen is excluded by maintaining a slight overpressure of coating gas in the chamber and by using purging ports at the entrance. The coating gas mixture is introduced through the untwisting nozzle and the vortex created untwists the yarn entering the chamber. Retwisting is accomplished with argon only at the exit nozzle. Yarn temperature is measured directly (optically) through a sight tube installed in the chamber wall.

Initial experiments showed that a considerably reduced gas flow (as compared to the resistance process) would be necessary in the radiant heating process. Since the radiation furnace is almost four times as long as the chambers used in the resistance process and only a light tension can be applied to the yarn to allow untwisting, a higher gas flow created a lateral oscillation or whipping motion which caused fraying and partial destruction of the yarn. The gas flow was reduced to the point where this did not occur and the methane concentration was adjusted to give concentrations between 15 and 120 parts per hundred parts of argon.

It was also found necessary to reduce the yarn speeds for the radiation heating process. Radiation heating is slower than resistance heating and requires more time for the yarn to reach the desired deposition temperature. With a tube temperature of 3000°C, the maximum practical yarn speed was 7 to 8 feet per minute for a yarn surface temperature of 2300°C.

A yarn speed of 7 feet per minute was selected for the first trials. Tests were run at deposition temperatures of 1800° to 2300°C with methane concentrations between 15 and 117 parts per hundred parts of argon. The results are shown in Figures 44 to 49. Although the tenacity gains were small, there was also no significant yarn deterioration at any of the process conditions investigated. With this apparatus oxidation was no longer a problem.

Another problem arose which seriously limits the usefulness of this type of equipment. Since only a very small gas flow could be used without causing oscillation of the yarn, the gas was quickly depleted of carbon molecules. Unlike the previous setups, the walls of the coating chamber were heated and therefore were likely sites for pyrolytic deposition. Since the walls were very much hotter than the yarn and presented a much greater area to be coated, a large proportion of available carbon was deposited on the tube walls. Poorest coating results were obtained at the highest deposition temperature, undoubtedly because the coating gas was already depleted of carbon before it reached a yarn section hot enough for useful deposition to take place. A further effect of the preferential deposition on the furnace walls is the eventual plugging of the tube with deposited carbon.



TUBE OD - 1.5 IN.
TUBE ID - 1.0 IN.
TUBE LENGTH-22.0 IN.

Figure 43. Yarn Coating Apparatus Based on Radiation Heating

L-1021

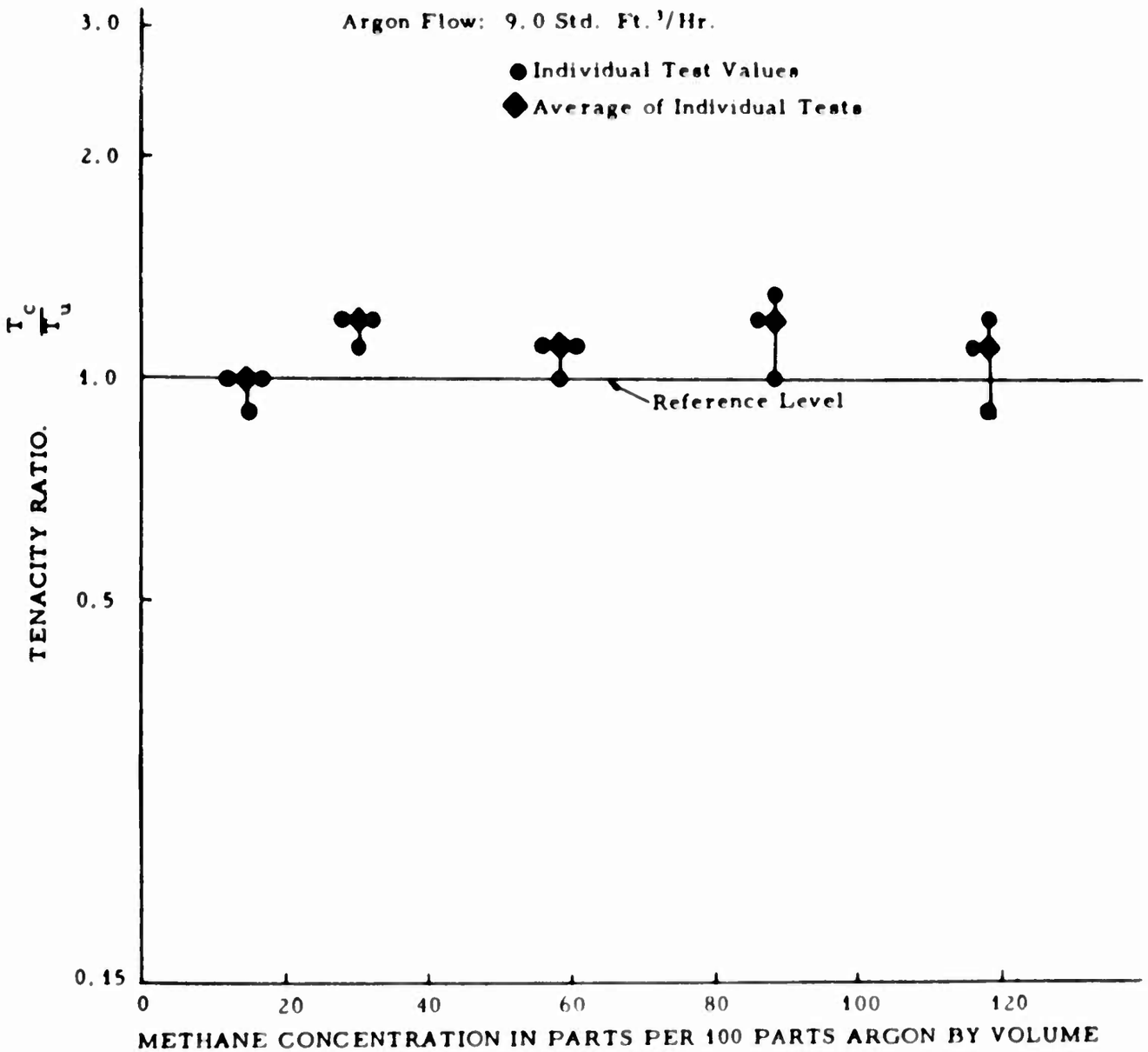


Figure 44. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 1800°C, Series 1: Yarn Speed of 7 Ft./Min. L-1022

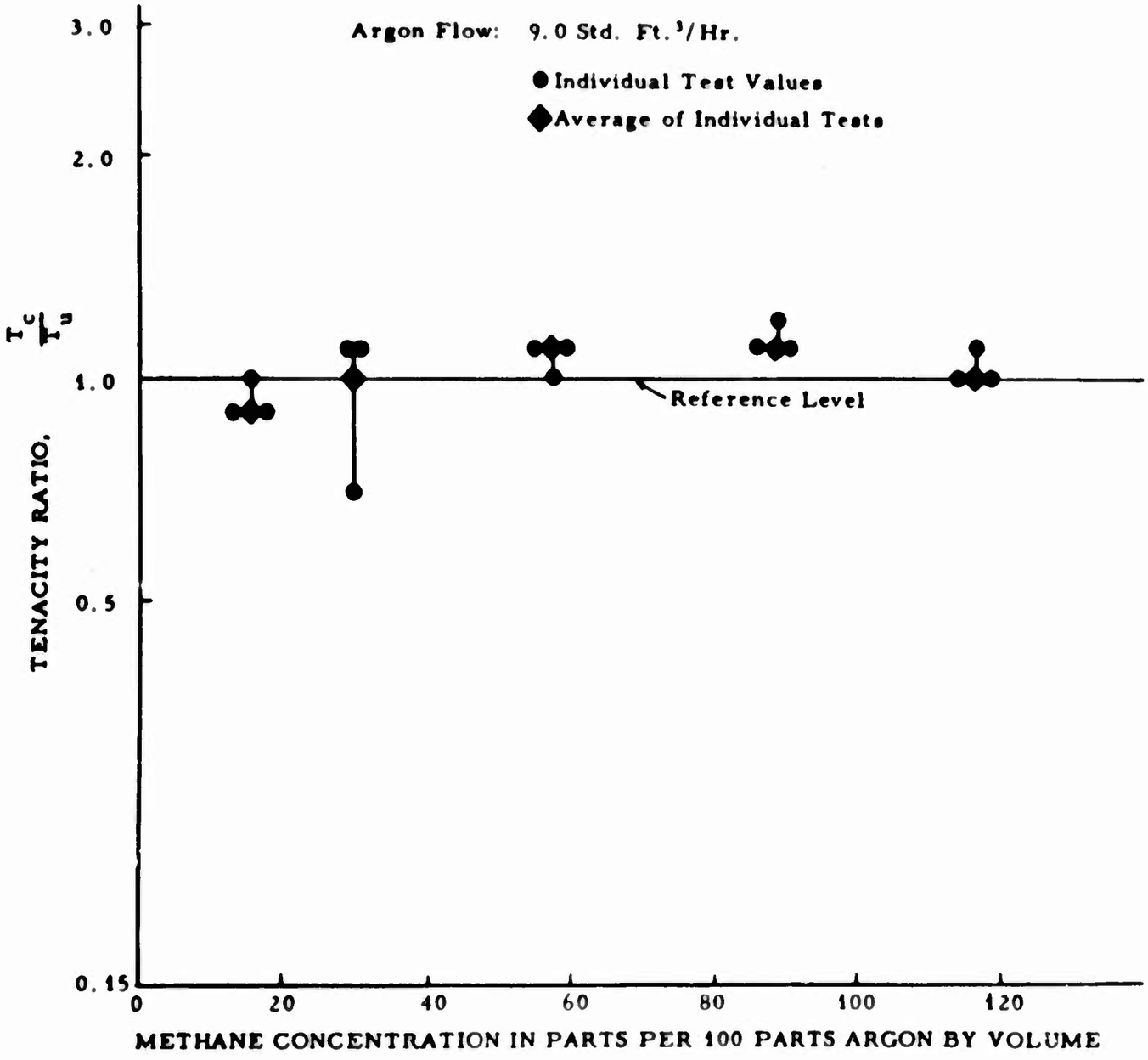


Figure 45. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 1900°C, Series 1: Yarn Speed of 7 Ft./Min.

L-1023

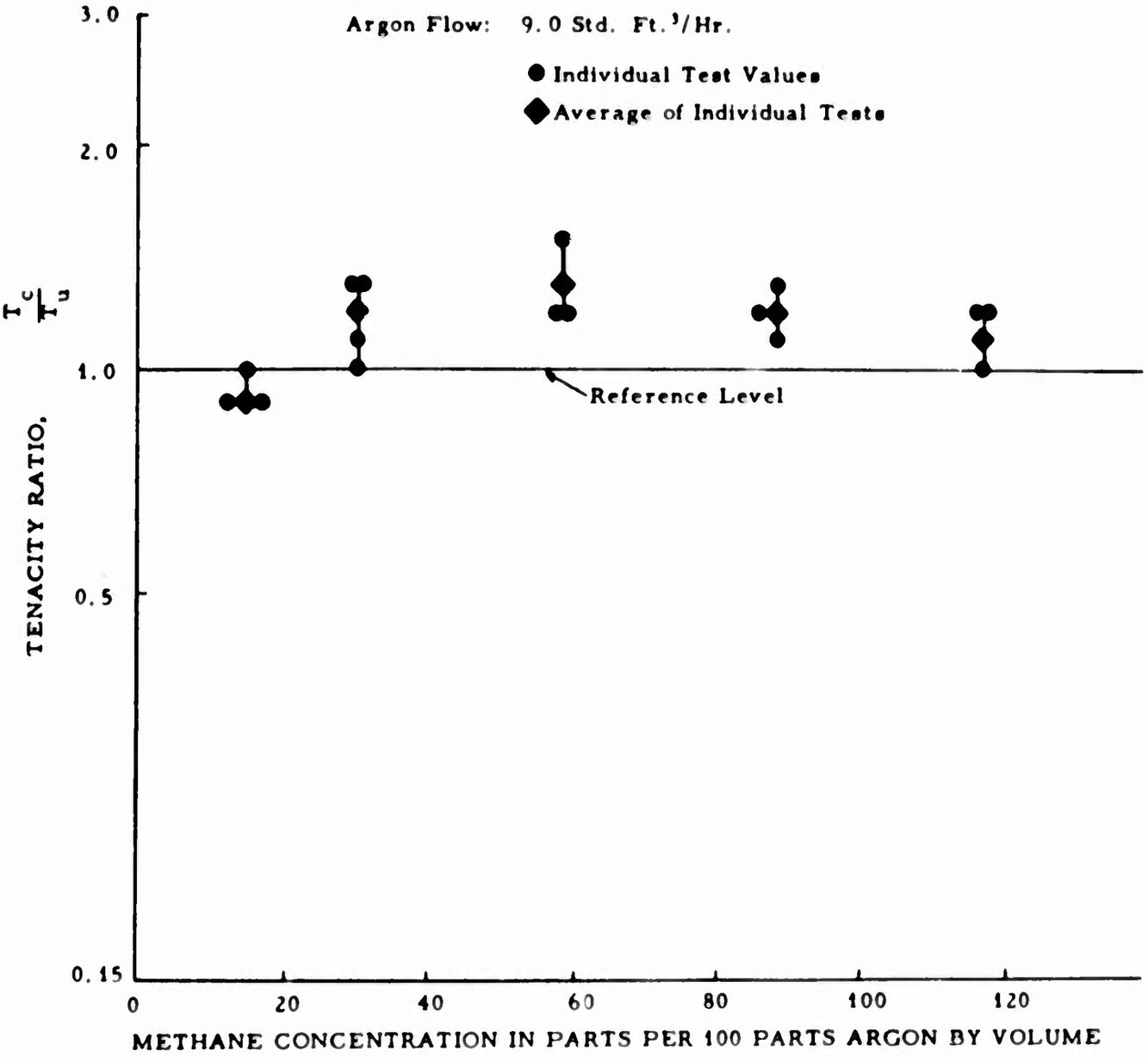


Figure 46. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2000°C, Series 1: Yarn Speed of 7 Ft./Min.

L-1024

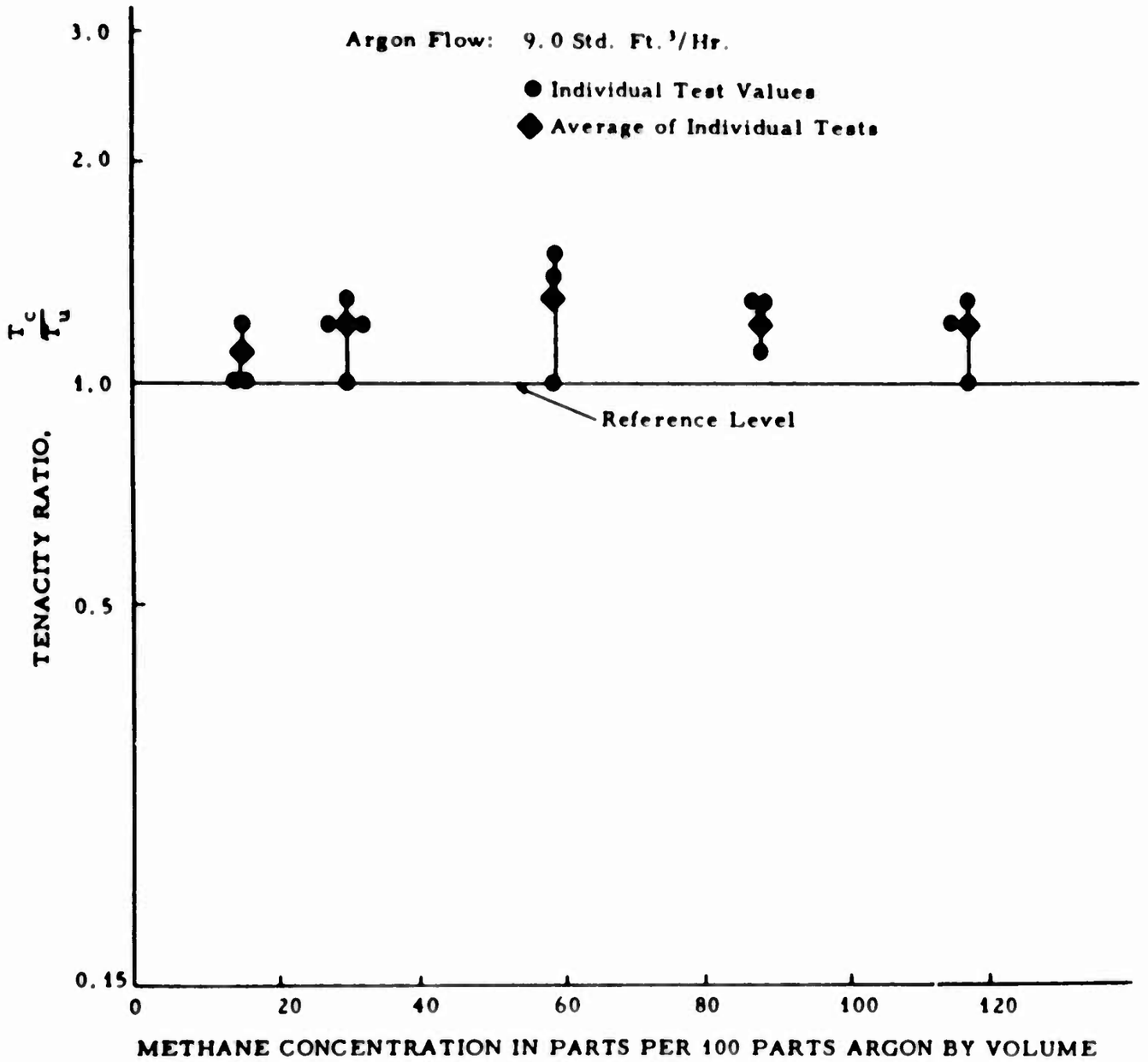


Figure 47. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2100°C, Series 1: Yarn Speed of 7 Ft./Min.

L-1025

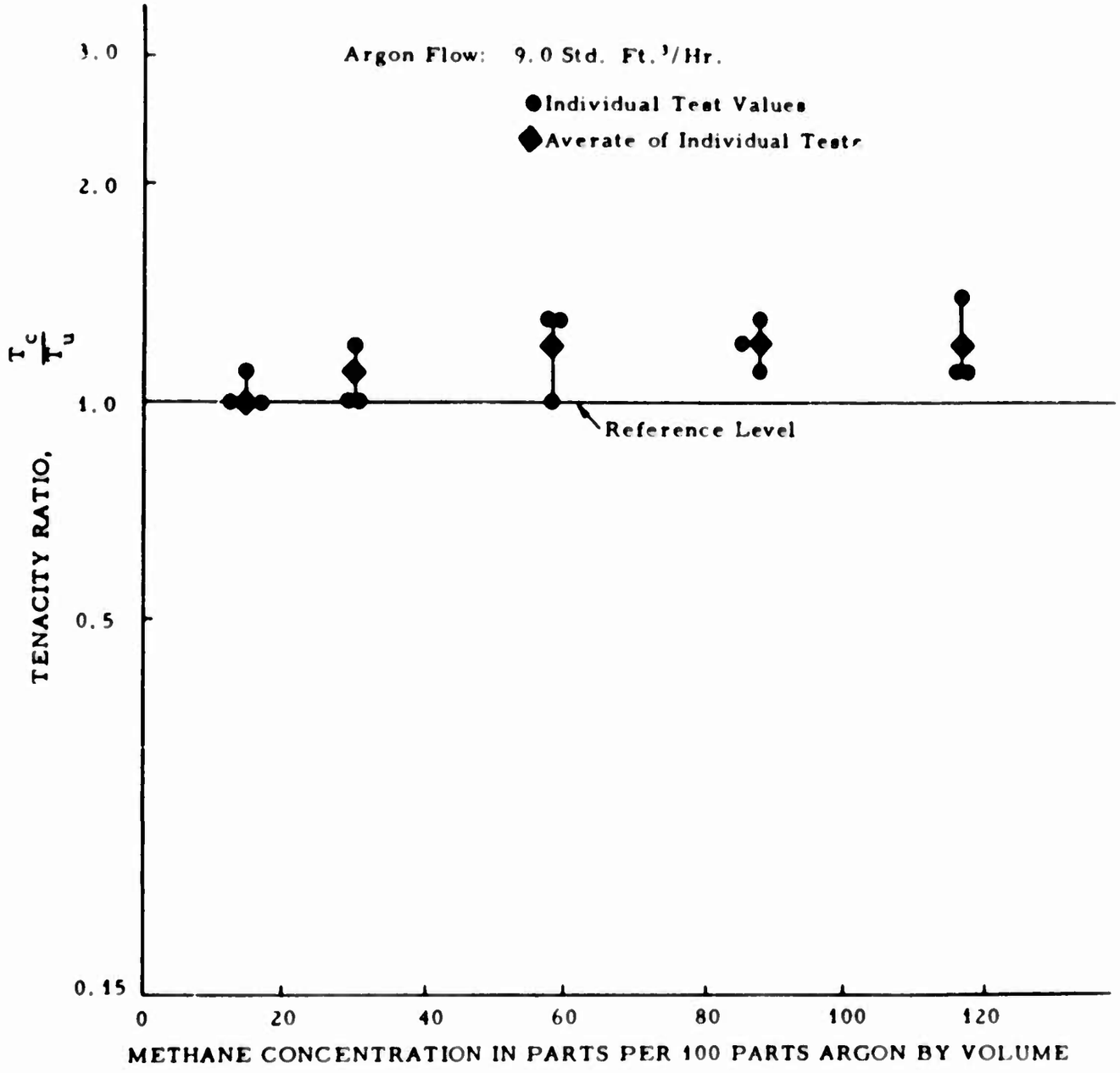


Figure 48. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2200°C, Series 1: Yarn Speed of 7 Ft./Min.

L-1026

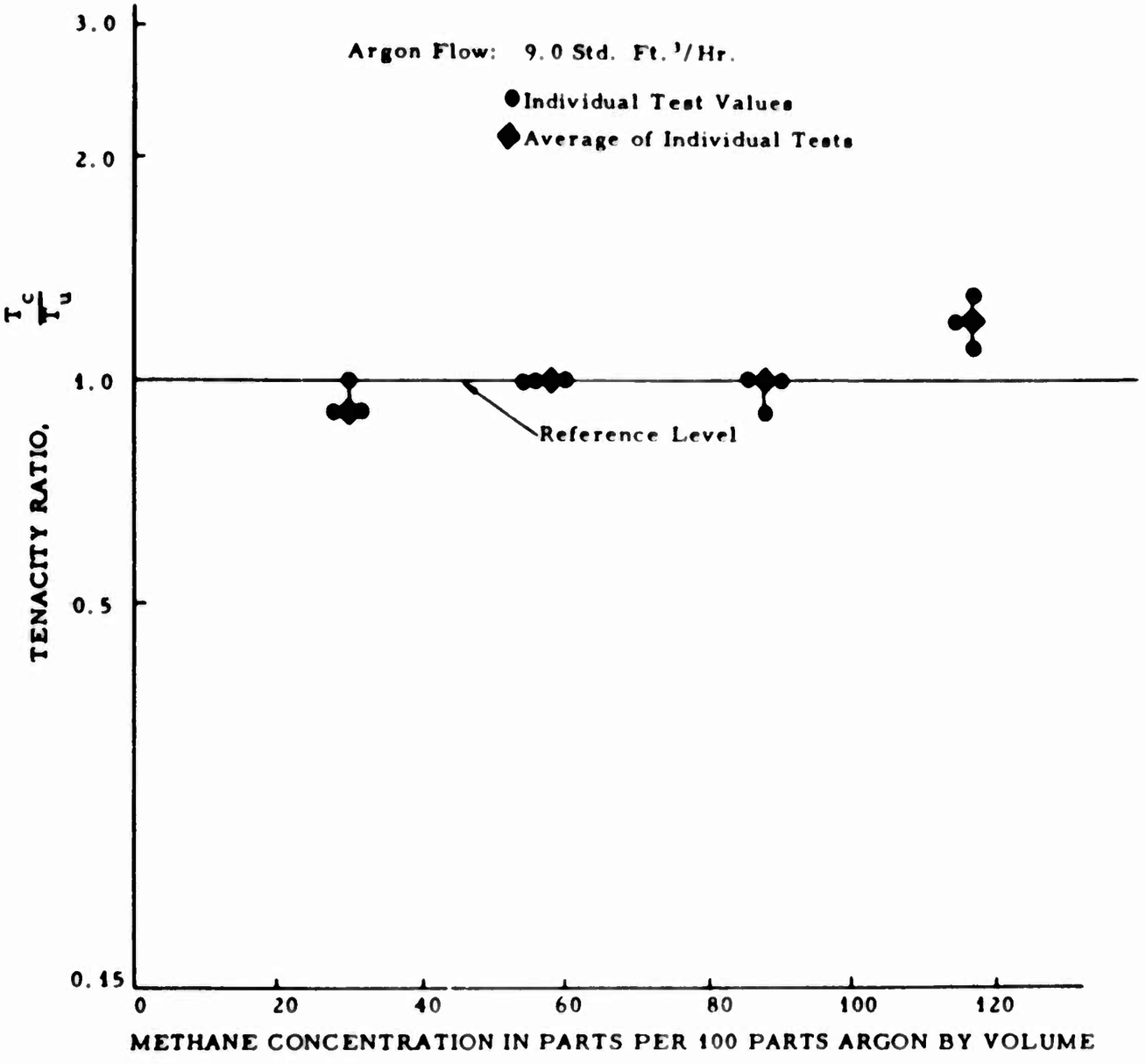


Figure 49. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2300°C, Series 1: Yarn Speed of 7 Ft./Min.

L-1027

Table 36. Data for Figure 44

UNCOATED YARN

Yarn Lot No.	3080
Average Pull Strength, Heat-Treated Form, lbs.:	5.6
Average Denier, Heat Treated Form, g/9000 M:	1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:	1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Agron	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
832	14.6	9.7	3	1580	5.5	1.6	1.0
833	29.2	11.0	3	1620	6.9	1.9	1.2
834	58.8	13.5	3	1700	6.7	1.8	1.1
837A	87.7	15.9	3	1830	7.8	1.9	1.2
838	117.0	18.4	3	1860	7.5	1.8	1.1

Table 37. Data for Figure 45

UNCOATED YARN

Yarn Lot No.	3080
Average Pull Strength, Heat-Treated Form, lbs.:	5.6
Average Denier, Heat Treated Form, g/9000 M:	1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:	1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
835	14.6	9.7	3	1540	5.2	1.5	0.9
836	29.2	11.0	3	1600	5.6	1.6	1.0
837B	58.8	13.5	3	1650	6.7	1.8	1.1
839	87.7	15.9	3	1780	7.0	1.8	1.1
843	117.0	18.4	3	1840	6.5	1.6	1.0

Table 38. Data for Figure 46

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Agron	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
840	14.6	9.7	3	1660	5.7	1.5	0.9
841	29.2	11.0	4	1610	7.0	1.9	1.2
845	58.8	13.5	3	1720	8.2	2.1	1.3
846	87.7	15.9	3	1830	8.4	2.0	1.2
847	117.0	18.4	3	1750	7.5	1.9	1.1

Table 39. Data for Figure 47

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.^{3}/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
848	14.6	9.7	3	1590	6.3	1.8	1.1
853	29.2	11.0	4	1650	7.2	2.0	1.2
854	58.8	13.5	3	1640	8.2	2.2	1.3
855	87.7	15.9	3	1740	7.6	2.0	1.2
856	117.0	18.4	3	1700	7.5	2.0	1.2

Table 40. Data for Figure 48

UNCOATED YARN

Yarn Lot No.	3080
Average Pull Strength, Heat-Treated Form, lbs.:	5.6
Average Denier, Heat Treated Form, g/9000 M:	1580 ±20
Average Tenacity, Heat Treated Form, g/denier,:	1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
857	14.6	9.7	3	1700	6.3	1.6	1.0
861	29.2	11.0	3	1670	6.6	1.8	1.1
862	58.8	13.5	3	1780	8.1	2.0	1.2
863	87.7	15.9	3	1815	8.1	2.0	1.2
864	117.0	18.4	3	1890	8.5	2.0	1.2

Table 41. Data for Figure 49

UNCOATED YARN

Yarn Lot No.	3080
Average Pull Strength, Heat-Treated Form, lbs.:	5.6
Average Denier, Heat Treated Form, g/9000 M:	1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:	1.6

COATED YARN

Yarn Speed: 7 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average, Tenacity g/denier	Tenacity Ratio
864A	14.6	9.7					
865	29.2	11.0	3	1770	6.2	1.5	0.9
866	58.8	13.5	3	1850	7.1	1.7	1.0
867	87.7	15.9	3	1860	7.0	1.7	1.0
868	117.0	18.4	3	1840	7.8	1.9	1.2

There is no wholly satisfactory solution to this problem. Increasing the diameter of the chamber also increases the ratio of wall surface to yarn surface. Decreasing the length of the chamber requires the yarn to be slowed down impractically if it is to reach deposition temperatures.

To investigate whether high tenacity gains could be achieved without major changes to the apparatus, a second test series was conducted at a speed of 4 feet per minute. This diminished speed allows a much smaller temperature differential to be maintained between the yarn and the chamber wall. The results of this series are presented in Figures 50 to 55. There seems to be a slight improvement in the tenacity over that obtained at 7 feet per minute.

One major conclusion that resulted from this study was that the slight oscillation of the yarn due to the length of the heated section and the reduced tension was found to be ideal for separating and uniformly coating all the filaments in the yarn.

3.3.3. Heating in a Plasma

To eliminate the drawbacks of both resistance and radiation heating, we tried a third process based on heating the yarn using the plasma of an induction torch illustrated in Figure 56. The torch consists of a quartz tube, a portion of which is surrounded by an induction coil connected to a radio frequency generator. Yarn and coating gas are passed through the quartz tube.

Operation is started by lowering a graphite "ignition ring" into the coil. It ionizes the ambient gas to bring the conductivity of the gas to a level here it is energized by the induction coil. The ignition ring can then be withdrawn, and the process begins as the yarn is heated by conductive contact with the hot plasma. Given enough power, speed of heating should be no problem, and the walls of the chamber can be cooled so that the drawbacks of the radiant heating process are circumvented.

The feasibility of the concept was investigated using a 10 KW, 3-megacycle generator at the Batelle Memorial Institute, Columbus, Ohio. Since it was not possible to install all of the process equipment and testing devices at Batelle, the evaluation of this process was based on visual examination of the yarn and the points studied were the behavior of the yarn within the plasma and the effect of adding methane to the plasma gases.

Normal deposition temperatures could be obtained when the yarn was passed through the plasma at speeds comparable to those used in the processes based on resistance heating, but the methane concentration of the coating gas was found to be limited by the power of the generator. Exceeding a methane level of 6 per cent by volume resulted in extinction of the torch. This indicates that above this critical value the requirement

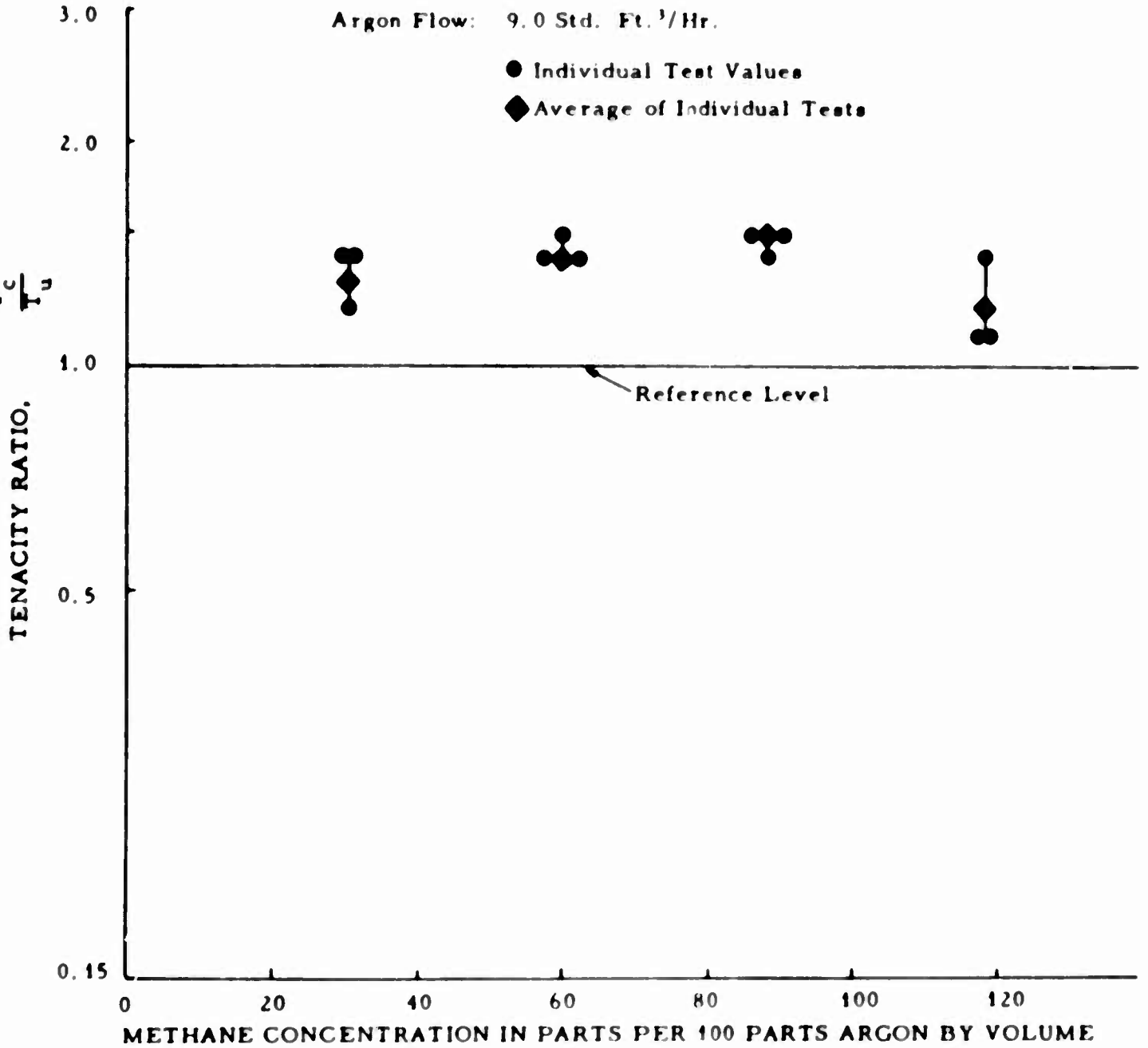


Figure 50. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 1800°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1028

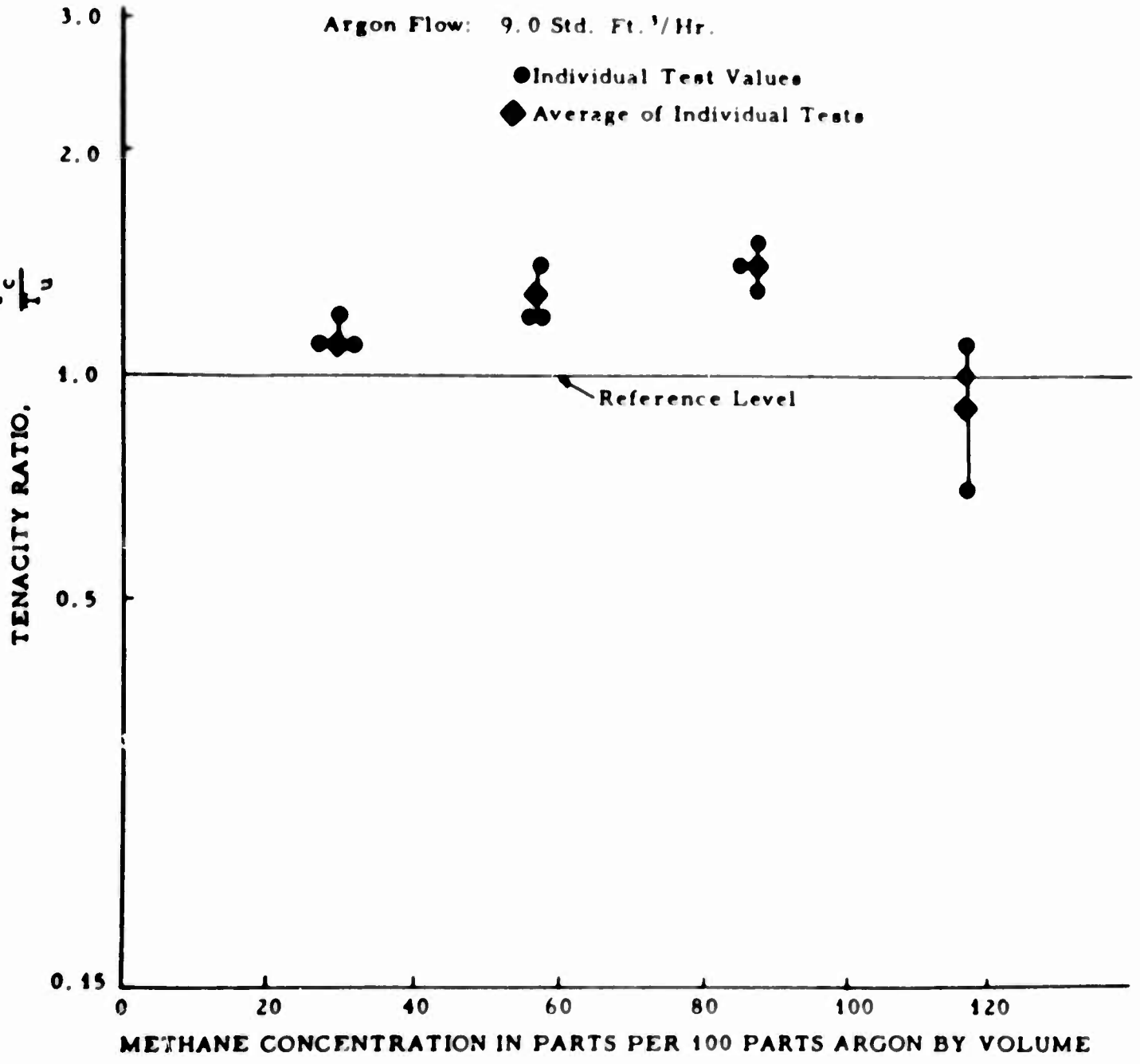


Figure 51. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 1900°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1029

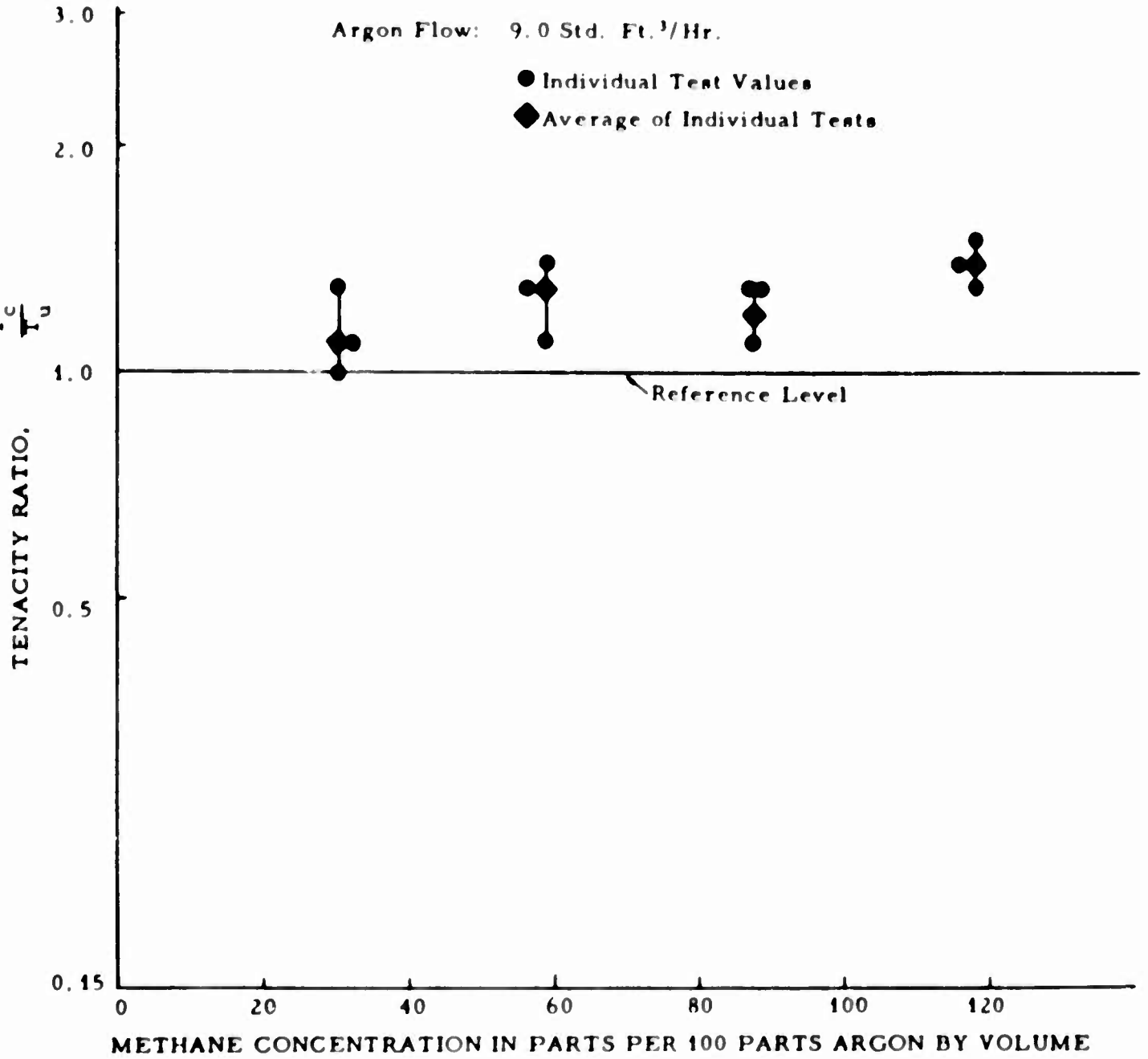


Figure 52. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2000°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1030

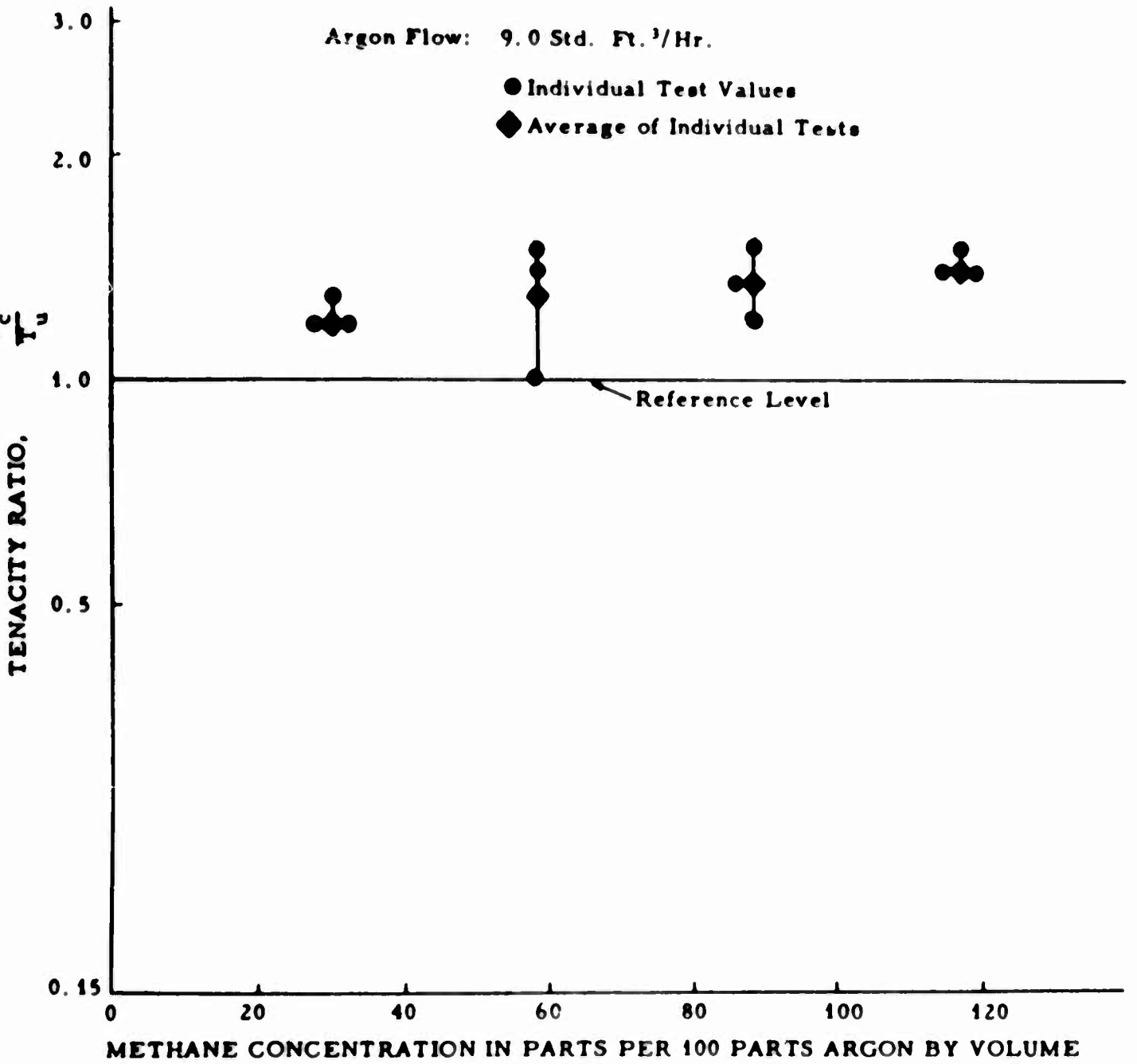


Figure 53. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2100°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1031

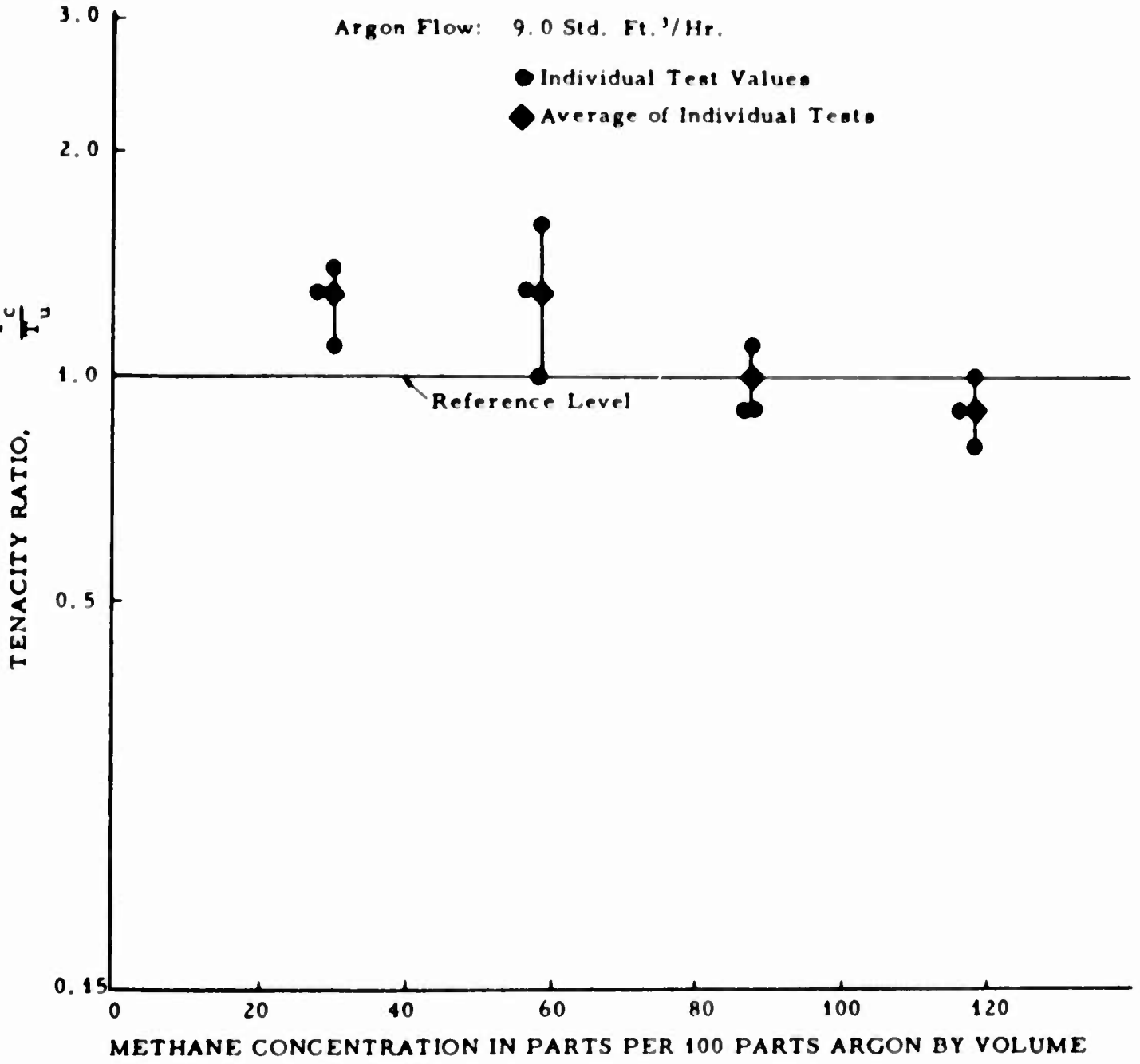


Figure 54. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2200°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1032

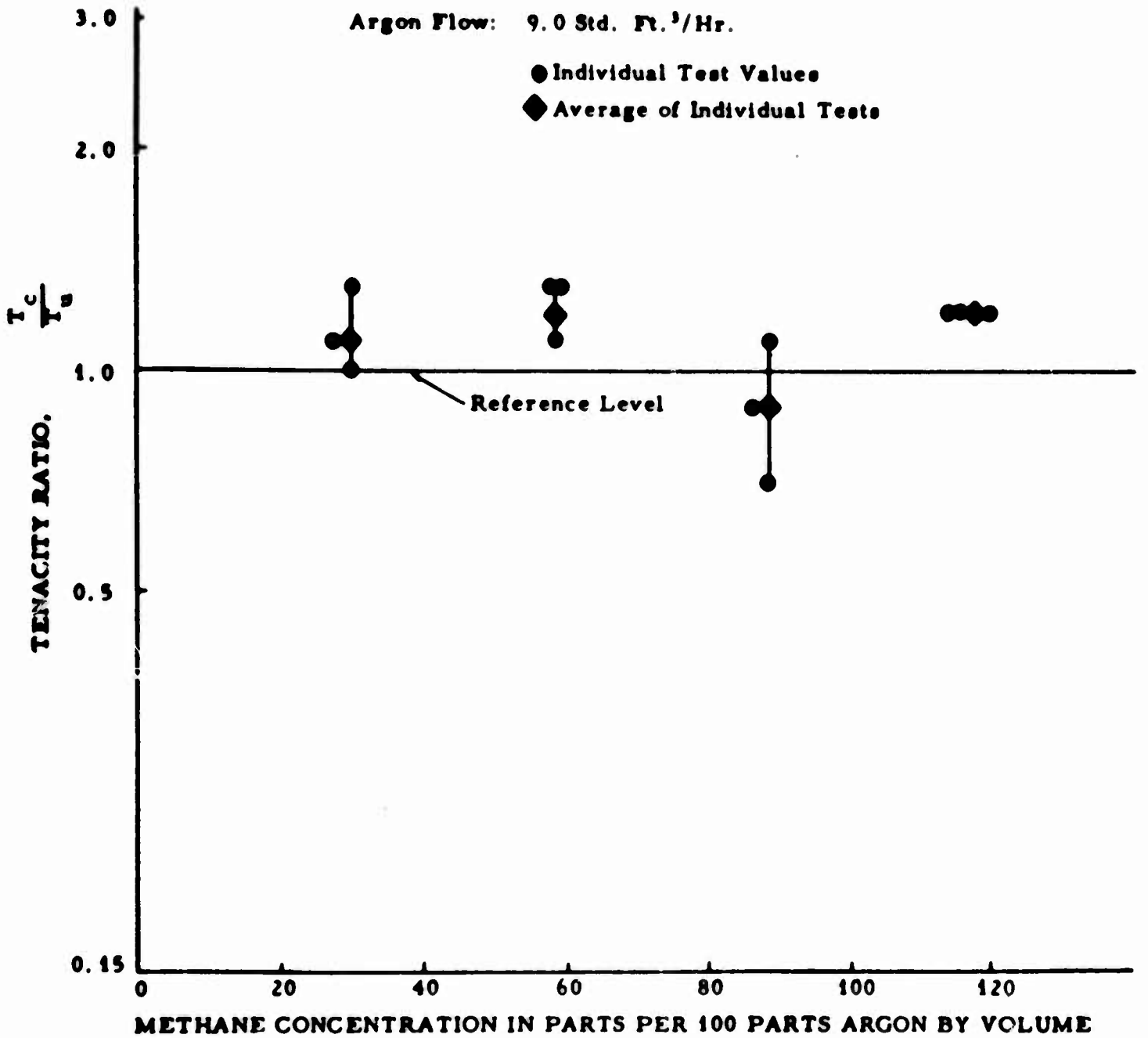


Figure 55. Tenacity Ratio of Yarn Coated in Radiative Chamber at a Deposition Temperature of 2300°C, Series 2: Yarn Speed of 4 Ft./Min.

L-1033

Table 42. Data for Figure 50

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat-Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
873	29.2	11.0	3	1880	9.0	2.1	1.3
874	58.8	13.5	3	1940	10.0	2.3	1.4
875	87.7	15.9	3	1920	10.1	2.4	1.5
876	117.0	18.4	3	2080	8.6	1.9	1.2

Table 43. Data for Figure 51

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
869	29.2	11.0	3	1840	7.5	1.8	1.1
870	58.8	13.5	3	2000	9.4	2.1	1.3
871	87.7	15.9	3	2040	10.4	2.3	1.4
872	117.0	18.4	3	2216	7.4	1.5	0.9

Table 44. Data for Figure 52

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN
Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.³/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
877	29.2	11.0	3	1790	7.1	1.8	1.1
878	58.8	13.5	3	1790	8.2	2.1	1.3
879	87.7	15.9	3	1840	8.3	2.0	1.2
880	117.0	18.4	3	1760	8.8	2.3	1.4

Table 45. Data for Figure 53

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN
Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. Ft.³/Hr.	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
881	29.2	11.0	3	1910	8.5	2.0	1.2
882	58.8	13.5	3	1950	9.1	2.1	1.3
883	87.7	15.9	3	2060	10.0	2.1	1.3
884	117.0	18.4	3	2240	11.5	2.3	1.4

Table 46. Data for Figure 54

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, t/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
885	29.2	11.0	3	1850	8.6	2.1	1.3
886	58.8	13.5	3	1670	7.9	2.1	1.3
887	87.7	15.9	3	2220	7.9	1.6	1.0
888	117.0	18.4	3	1940	6.3	1.5	0.9

Table 47. Data for Figure 55

Yarn Lot No.	UNCOATED YARN	3080
Average Pull Strength, Heat-Treated Form, lbs.:		5.6
Average Denier, Heat Treated Form, g/9000 M:		1580 ± 20
Average Tenacity, Heat Treated Form, g/denier,:		1.6

COATED YARN

Yarn Speed: 4 Ft./Min.

Expt. No.	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr.$	No. of Samples	Average Denier, g/9000m	Avg. Pull Strength lbs.	Average Tenacity g/denier	Tenacity Ratio
889	29.2	11.0	3	1990	8.2	1.8	1.1
890	58.8	13.5	3	2140	9.6	2.0	1.2
891	87.7	15.9	3	2220	7.3	1.5	0.9
892	117.0	18.4	3	1760	7.5	1.9	1.2

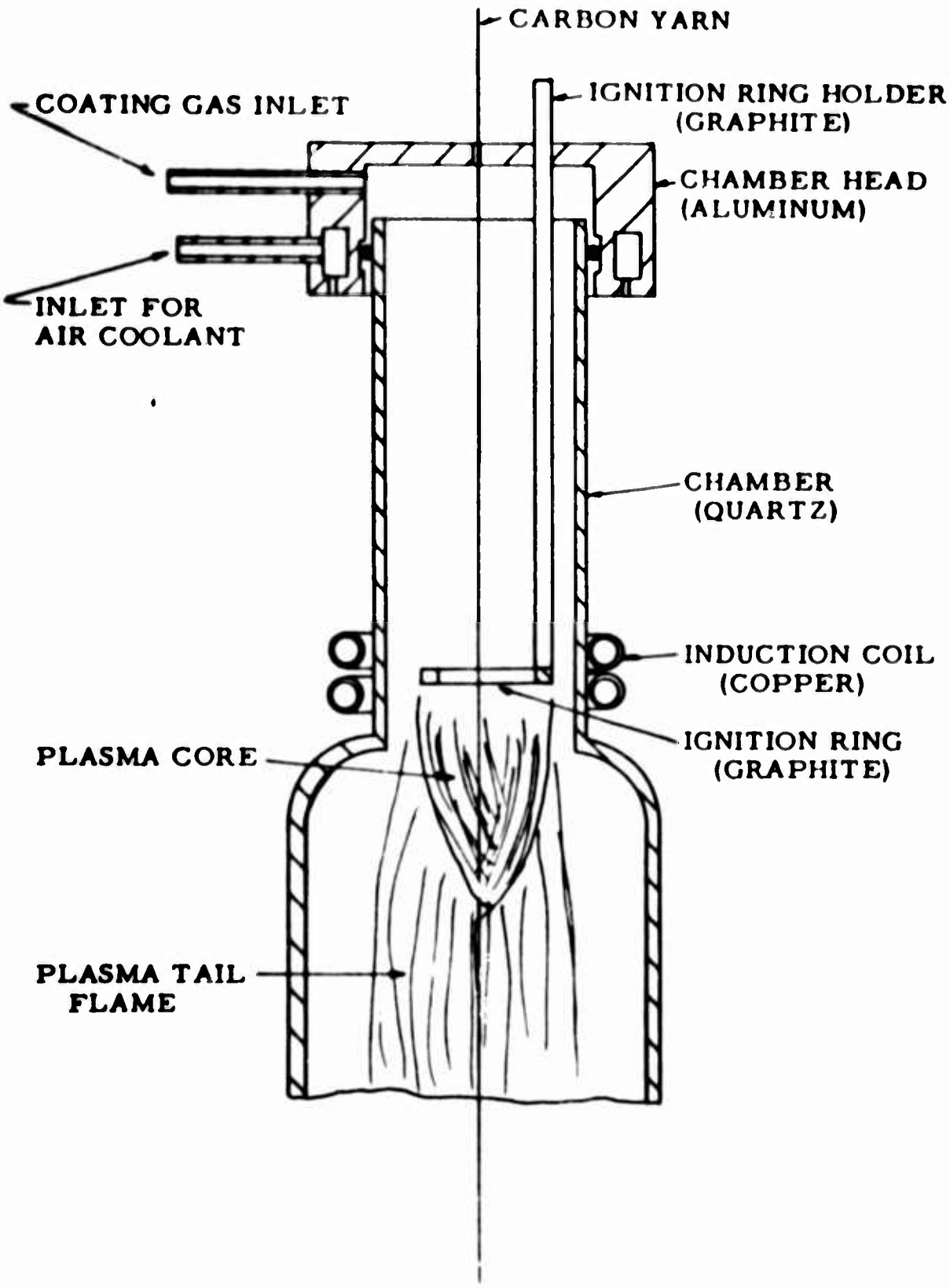


Figure 56. Coating Chamber Based on Conductive Heating.

L-1034

for power to ionize the hydrocarbon exceeded the power available. The use of larger power sources should increase the permissible methane concentration.

At the highest methane level, a thin pyrolytic coating was deposited on the yarn. The yarn itself was unaffected by passing through the plasma. Experiments showed that residence time was no problem since the yarn could remain within the plasma for 15 seconds before it was vaporized.

No hard carbon deposit was formed on the walls of the quartz chamber. There was some soot deposited on the walls but since this affects only the heat transfer through the walls of the tube it had no bearing on the coating process itself.

Although it was evident that greater methane concentrations would be necessary to obtain any significant amount of pyrolytic graphite deposition, in principle, the process is worthy of further investigation since it has none of the drawbacks inherent in the other methods tried.

3.4. Penetration Studies

Throughout this investigation, continuous attention was devoted to uniformly coating all of the filaments in the yarn. Since this is one of the goals of the program, the subject is treated here separately.

Samples of the coated yarn were mounted and their cross sections examined by metallographic techniques to determine the uniformity of the coating throughout the filaments. The first carbon yarns in which all of the filaments were uniformly coated were processed in the radiation furnace. An example of this material, coated at 2100°C with a methane concentration of 118 parts per 100 parts of argon and a yarn speed of 4 ft./min., is shown in Figure 57.

In examination of the radiation process to determine the reason for the uniform coating on the filaments, attention was focused on the method of filament separation. Since the length of yarn within the radiation chamber was almost four times that used in the resistance furnace, some lateral oscillation (vibration) developed in the yarn even at the relatively low gas flow rates used during coating. These vibrations were apparently much more effective for separating the filaments than any method previously used.

Similar vibrations were induced in the yarn in the resistance apparatus by reducing the tension on the yarn from 220 to 90 grams and removing the vortex nozzles.

Trials were made at several different methane concentrations while keeping the filament speed constant at 25 ft./min. and the argon flow constant at 34 std. ft.^{3}/hr. Deposition temperatures were varied from 1900° to 2200°C. Samples of the material produced were examined

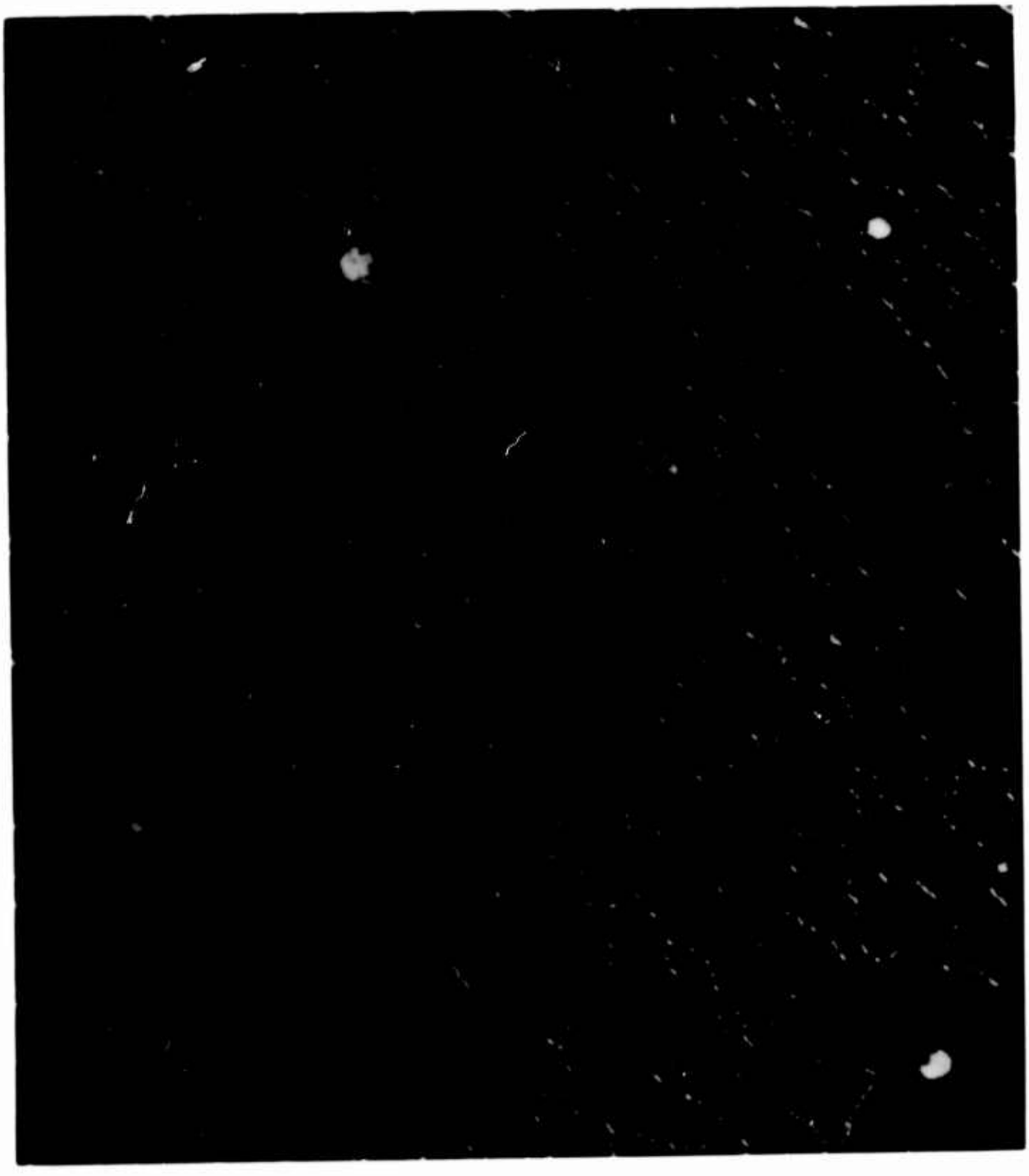


Figure 57. Cross Section of Carbon Yarn After Processing in the Radiation Furnace:
Deposition Temperature - 2100°C
Yarn Speed - 4 Ft./Min.
Methane Concentration - 118 Parts/100 Parts Argon by Volume
Argon Flow Rate - 9 Std. $Ft.^3/Hr.$ (1000X)

microscopically to determine the amount of coverage achieved. Complete coverage of the filaments was obtained at a deposition temperature of 1900°C and a methane concentration of 88 parts per 100 parts of argon. Figure 58 is a cross section view of a sample of yarn coated at 1900°C and 88 parts methane per 100 parts of argon at 25 ft./min. using Chamber B. Uniform coatings could also be obtained at higher deposition temperatures and higher methane concentrations. The higher deposition temperatures caused an increased thickness of coating and a much stiffer yarn. Higher methane concentrations resulted in the deposition of soot on the surface of the yarn plies. These results show that one of the primary factors controlling the uniformity of the coatings on the individual filaments is the efficiency of separation of the heated filaments while they are in contact with the carbonaceous gas.

The uniformity of the coating around the individual filaments is shown in the surface replica in Figure 59. This is a picture at 16,000X made on an electron micrograph. The apparent distinction between inner and outer coatings is an artifact. Rather, these are etch lines between the mounting plastic and the coating and between the coating and the filament. These lines are due to local electric fields created by the different materials and are a function of time; i.e., an etch "front" appears to proceed, for example, from the outside of the coating toward the inside boundary. This picture, which is representative of all the filaments studied, shows that there is no delamination within the coating, that it is complete, and that it is generally uniform around any one filament. There always exists, however, a very small crack between the filament core and the coating which is due to differential shrinkage.

This series of experiments led to the establishment of standard operation conditions for the production of pyrolytically-coated carbon yarn. These conditions are:

Chamber Design	B
Methane Concentration in Coating Gas	88 parts/100 parts argon
Total Gas Flow	64 std. ft.^{3}/hr.
Filament Speed	25 ft./min.
Heating	By resistance
Deposition Temperature	1900° to 2200°C

Uniform coverage of all the filaments could be obtained at a deposition temperature of 1900°C. Increasing the deposition temperature resulted in thicker coatings being applied to the filaments. Therefore, the deposition temperature is dependent on the amount of stiffness required in the final coated yarn. The material produced at 1900°C was flexible and suitable for applications such as weaving or filament winding, while that produced at 2200°C was stiffer and more brittle, making it suitable for inclusion in bulk materials.

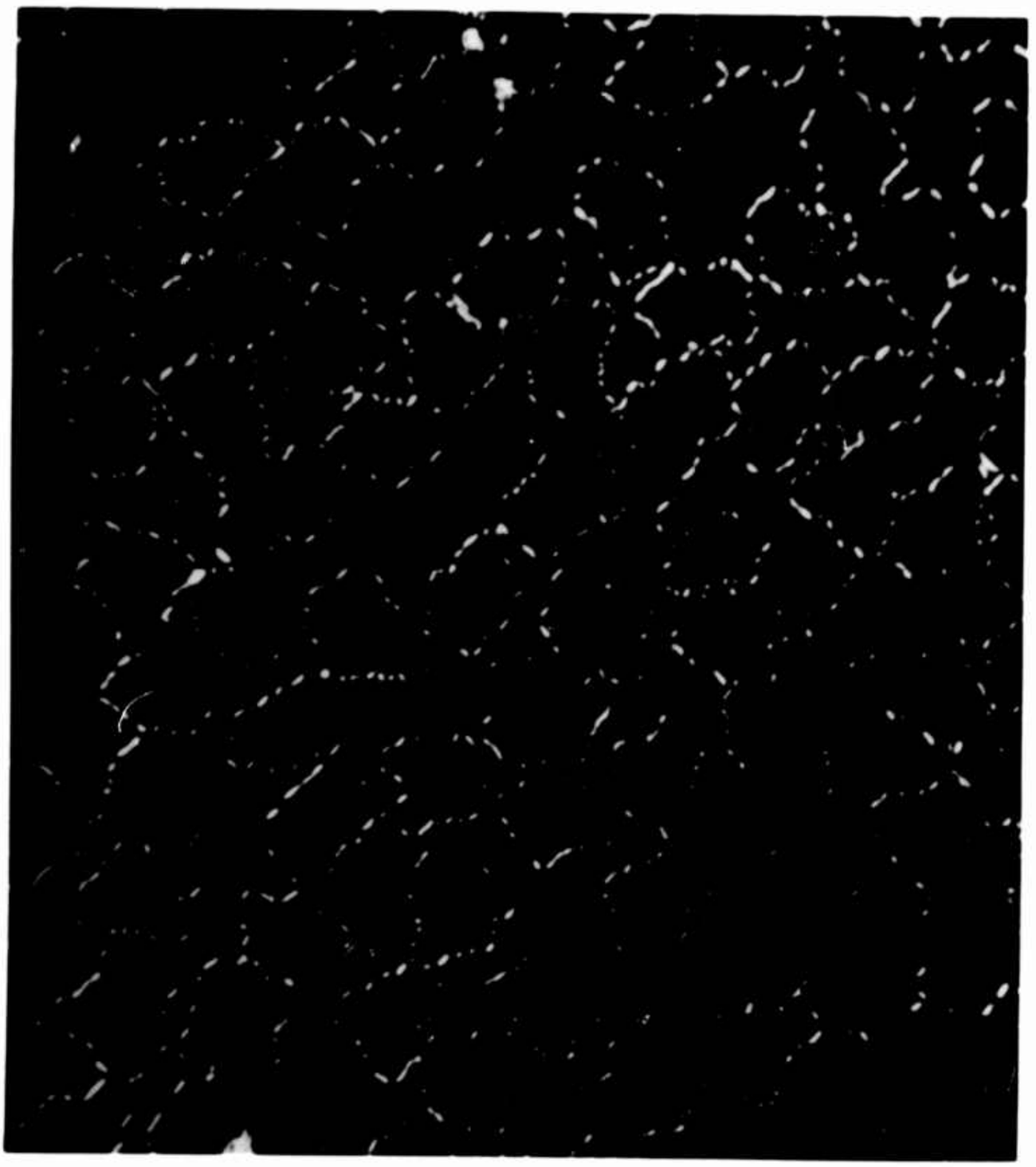


Figure 58. Cross Section of Carbon Yarn After Processing by Resistance Heating in Chamber C:
Yarn Tension - 90 grams
Deposition Temperature - 1900°C
Yarn Speed - 25 Ft./Min
Methane Concentration - 88 Parts/100 Parts Argon by Volume
Argon Flow Rate - 34 Std. $Ft.^3/Hr.$ (1200 X)

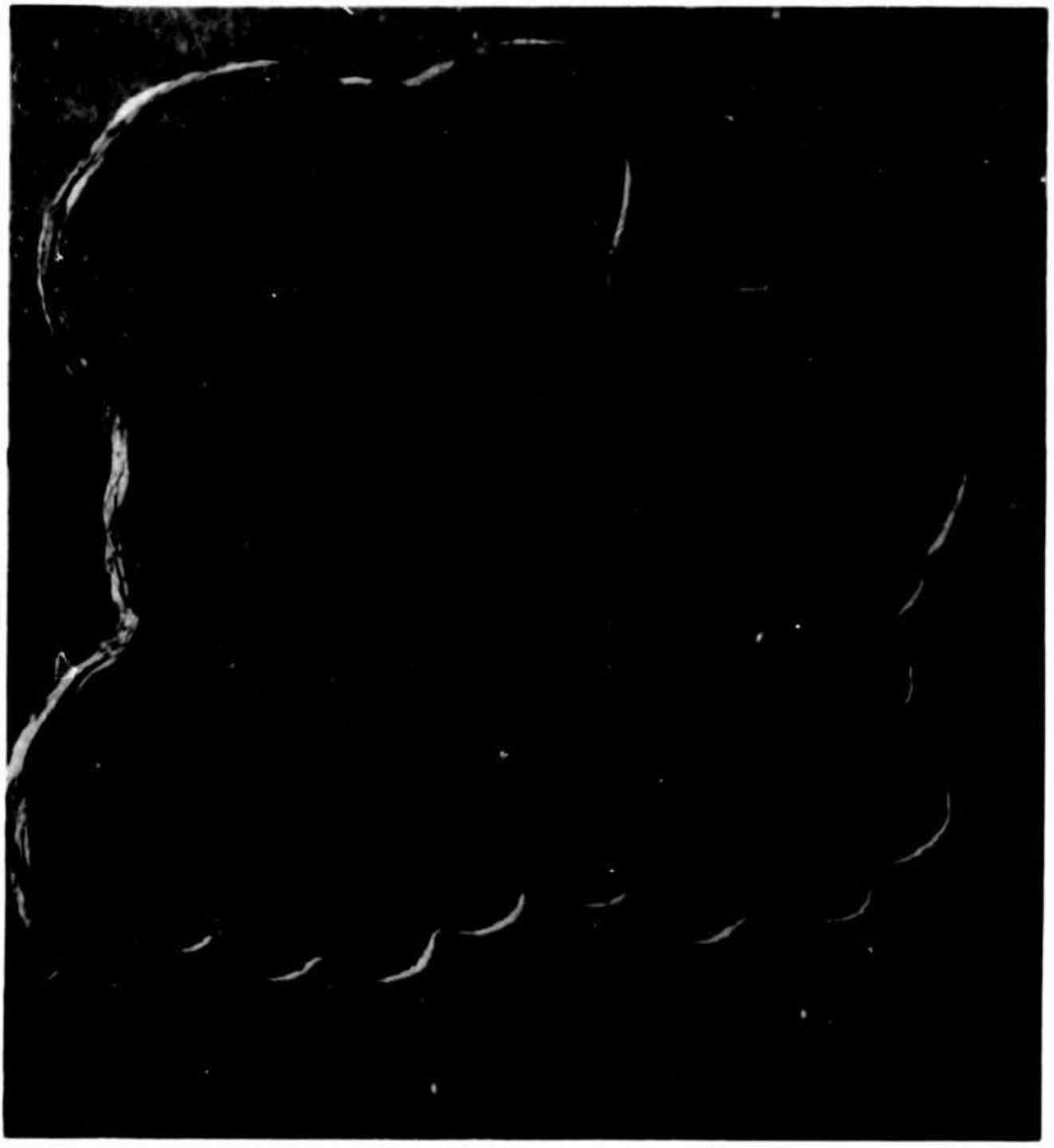


Figure 59. Cross Section of Coated Carbon Filament, Carbon Replica as Viewed in an Electron Microscope, Magnification: 16,000 X

3.5. Evaluation of Resistance Heating in Vacuo

A principal problem associated with the coating processes based on resistance heating was oxidation. To overcome this problem, the complete apparatus was mounted in an atmosphere-controlled vessel.

3.5.1. Heat-Treatment in Vacuo

The resistance equipment was installed in a vacuum chamber and the pressure was reduced to 0.3 Torr, the chamber was then filled with argon and pumped down again to 0.3 Torr. The yarn was then heated to 1900°C to effect further carbonization. This procedure was followed at several pressure levels between 0.3 and 720 Torr. It was found that at the pressures below 720 Torr, the carbonization process was too rapid, resulting in excessive weakening of the yarn. However, at 720 Torr, the tenacity of the heat-treated yarn averaged 20 per cent higher than that heat-treated at atmospheric pressure using the gas sheath to protect the yarn from oxidation. (See Table 48.) These results indicate that reduced pressure is not of any benefit in itself but that the increased protection from oxidation achieved in the inert atmosphere of the vacuum chamber accounted for the difference in tenacity levels obtained during the heat-treatment.

Table 48. Comparison of the Tenacities of Yarn Heat-Treated at Reduced and at Ambient Pressures

Pressure	Atmosphere	Speed	Temperature	Tenacity	Avg. Tenacity
720 Torr	Argon	25 Ft./Min.	1900°C	1.4 1.8 1.9 1.8 1.8 1.8	1.8
Ambient	Argon	25 Ft./Min.	1900°C	1.7 1.8 1.9 1.4 1.0 1.1	1.5

3.5.2. Coating in Vacuo

Using carbon yarn heat-treated as described above, several coating trials were made at various pressure levels between 0.3 and 720 Torr. The same procedure of pumping, flushing and repumping was used during the coating trials as was used in the heat-treating experiments.

The standard coating conditions as determined by the penetration, were used in this investigation (Section 3.4.).

The results of this investigation were as follows: At a pressure of 0.3 Torr, only a very small coating gas flow rate could be tolerated, otherwise violent vibration of the yarn occurred between the contact wheels. This caused the yarn to strike the sides of the coating chamber which resulted in destructive arcing. When the coating gas flow was reduced to the point where this vibration was not significant, the gas did not penetrate the yarn and only the surface filaments were coated. Experiments were conducted at various pressure levels, and it was found that at 720 Torr, the coating gas flow could be increased to the normal flow of 64 std. $ft.^3/hr.$ and complete penetration and therefore uniform coating of the filaments could be obtained.

No significant difference in tenacity was apparent between the tenacity of the yarns obtained by coating at reduced pressure and those obtained at atmosphere pressure, as shown in Table 49. This means that heat-treated yarn is not as sensitive to oxidation as the nonheat-treated yarn and that the gas sheath provided by the coating gases is sufficient to protect it from oxidation.

Because of time limitations, other gas flow rates were not tried.

Table 49. Comparison of the Tenacities of Heat-Treated Yarn Coated at Ambient and Reduced Pressures

UNCOATED YARN

Yarn Lot No. 12.21

Average Pull Strength, Heat-Treated Form, lbs.: 6.8

Average Denier, Heat Treated Form, g/9000 M: 1720

Average Tenacity, Heat Treated Form, g/denier,: 1.8

COATED YARN

Yarn Speed: 25 Ft./Min.

Pressure Torr	Meth. Conc., Parts/100 Parts Argon	Total Gas Flow Rate, Std. $Ft.^3/Hr$	Atmosphere	Temperature °C	Tenacity g/denier	Average Tenacity
720	88	64	Argon	1900	2.1 1.8 2.6 2.0 2.1 2.4	2.2
Ambient	88	64	Argon	1900	1.9 1.8 1.6 2.4 2.5 2.4	2.1

3.6. Statistical Characteristics of Pull Strength Variations

Evaluation of pyrolytically-coated carbon filaments frequently revealed variations which could not be accounted for by changes in the process conditions. It was theorized that inconsistencies of this type were likely to result from variations in the uncoated yarn as all yarn used in this study was made on experimental equipment.

Some of the scatter observed was serious enough to obstruct recognition of genuine process effects. A study was initiated to determine the statistical pattern of the variations encountered and to use such findings for final coating condition evaluations.

Since the denier within each lot of yarn remains fairly constant, the pull strength was considered to be the probable source of the variations.

The first part of the study was aimed at integral pull strength variations in the as-received material as a function of the length in any typical ball of yarn. Using a 2-pound ball, representing approximately 4500 yards, the first 650 yards were tested. Sampling frequency and results are compiled in Table 50.

It is readily seen that apart from scatter within a short length of yarn, there are also significant variations of both strength average and relative dispersion. It appears advisable for coating studies to work with short yarn sections, to extensively sample the yarn adjacent to the coated material, and to repeat application of the same coating conditions in order to check the reproducibility of the process. An example of this procedure is illustrated in Figure 60 where yarn strengths are plotted versus the length coordinate with coated and uncoated sections alternating. In spite of a pronounced variation of the group averages, an overall superiority of the coated product over the raw material is apparent. However, the results of the investigation cannot be characterized in numerical terms from this type of curve. To analyze the data, since the variations of group averagrs do not exhibit any prevailing trend upward or downward, we considered it justified to combine the individual values of a minimum number of frequency polygons pertaining to coated and uncoated materials.

The results of such studies are shown in Figures 61 to 64, representing the effect of favorable coating conditions with deposition temperatures between 1900° and 2200°C. The deviations from normal Gaussian distributions are expressed in terms of skewness of zero and a moment coefficient of kurtosis of three, the actual distributions are seen to be sufficiently close to normal to justify the procedure.

In summary, the findings allow clear separation of scatter from genuine effects of processing. For the particular combination of yarn and process investigated, the application of pyrolytic coatings was found capable of reliably increasing the average integral pull strength of the yarn by up to 40 per cent.

Table 50. Integral Pull Strength Variation in Raw Carbon Yarn

Length Coordinate Range, yards	Sampling Frequency	Number of Samples	Average Integral Pull Strength Within Each Group, lbs.	Standard Deviation Within Each Group, lbs.	Relative Dispersion Within Each Group, per cent	Average Integral Pull Strength of All Tests, lbs.	Standard Deviation for All Tests Combined, lbs.	Relative Dispersion for All Tests Combined, per cent
0 to 50	One 18" Specimen Every 18 inches	95	11.2	4.0	35.7	11.7	4.0	34.2
50 to 150	One 18" Specimen Every 36 inches	98	14.7	3.3	22.4			
150 to 650	One 18" Specimen Every 180 inches	99	9.2	2.3	25.0			

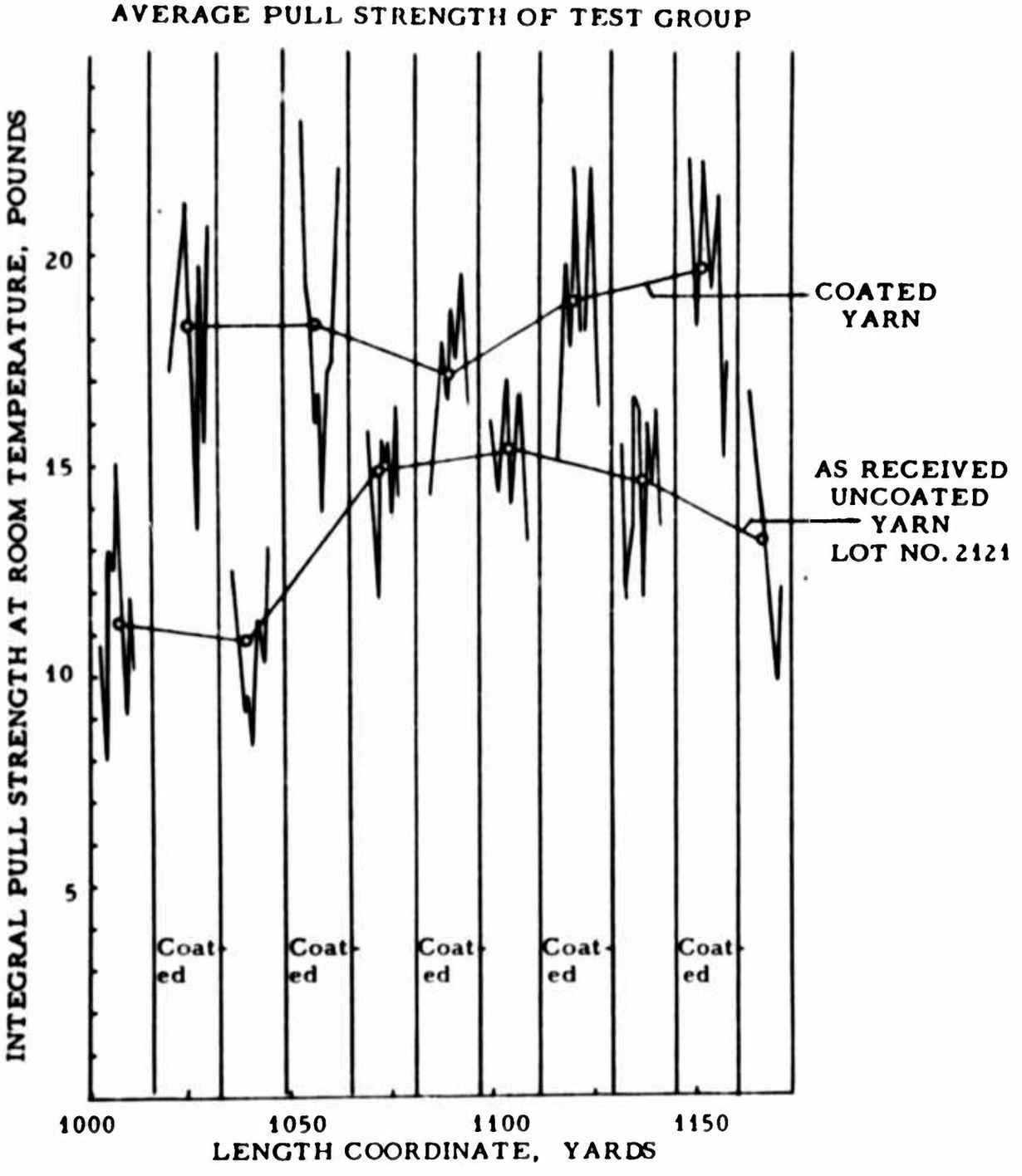


Figure 60. Coating Evaluation, Chamber B, 1900°C

L-1038

Table 51. Data for Figure 60

Yarn Processing History Lot No. 2121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2022	Uncoated				10	2225	11.2	2.3	
2023	1900	25	88	63.4	10	2200	18.3	3.8	1.7
2024	Uncoated				10	2180	10.8	2.3	
2025	1900	25	88	63.4	10	2230	18.4	3.7	1.4
2026	Uncoated				10	2190	14.9	3.1	
2027	1900	25	88	63.4	10	2230	17.2	3.5	1.1
2028	Uncoated				10	2180	15.4	3.2	
2029	1900	25	88	63.4	10	2290	18.9	3.8	1.2
2030	Uncoated				10	2200	14.6	3.0	
2031	1900	25	88	63.4	10	2250	19.7	4.0	1.4
2032	Uncoated				10	2210	13.1	2.7	

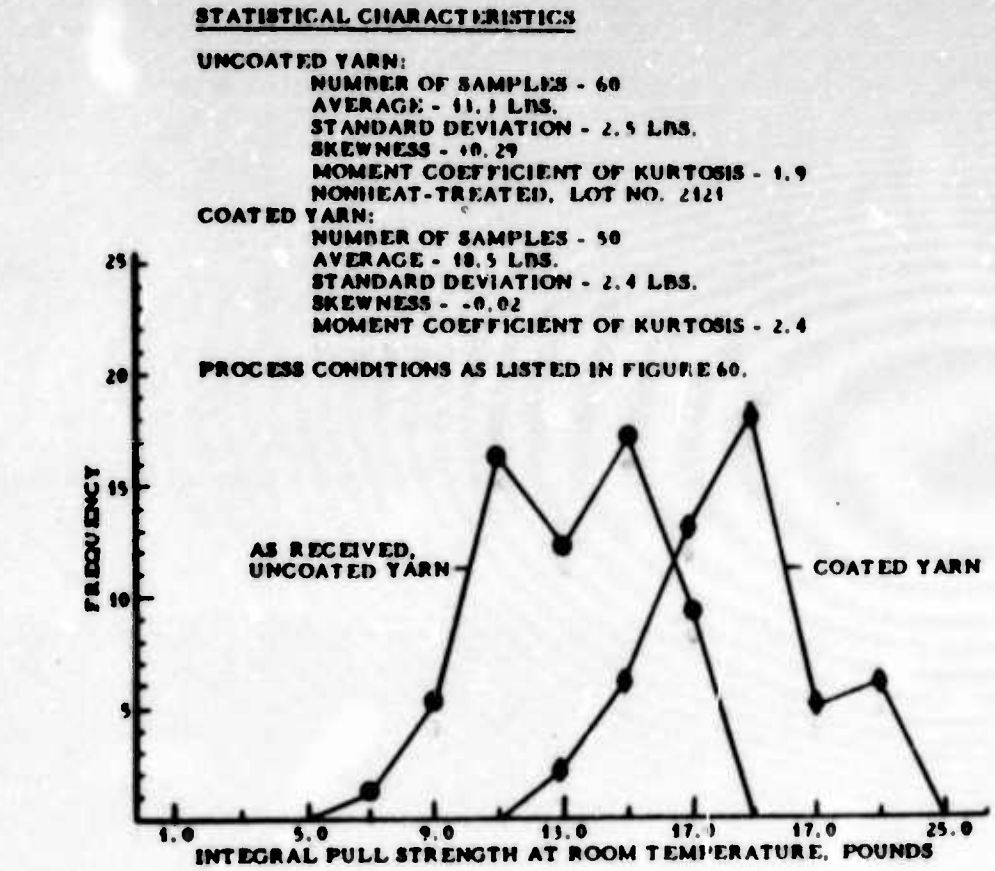


Figure 61. Frequency Polygon Comparison Between As Received Uncoated Yarn and Yarn Pyrolytically Coated at 1900°C

L-317

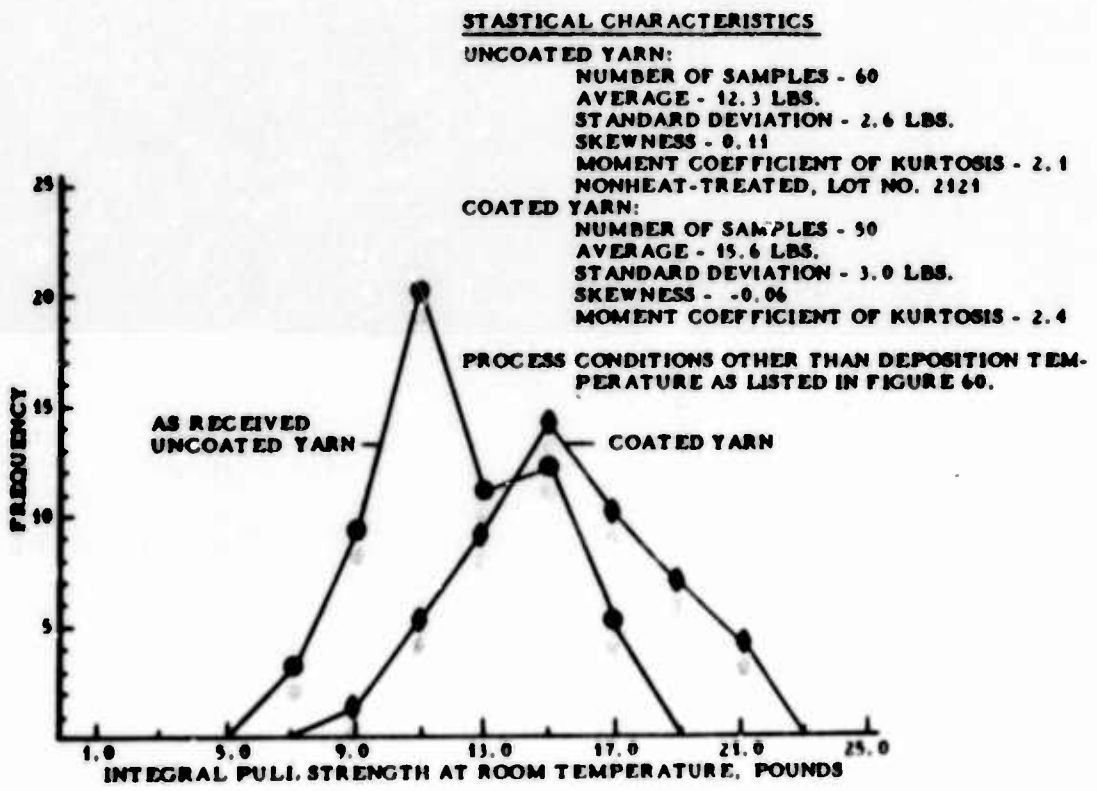


Figure 62. Frequency Polygon Comparison Between As Received Uncoated Yarn and Yarn Pyrolytically Coated at 2000°C

L-318

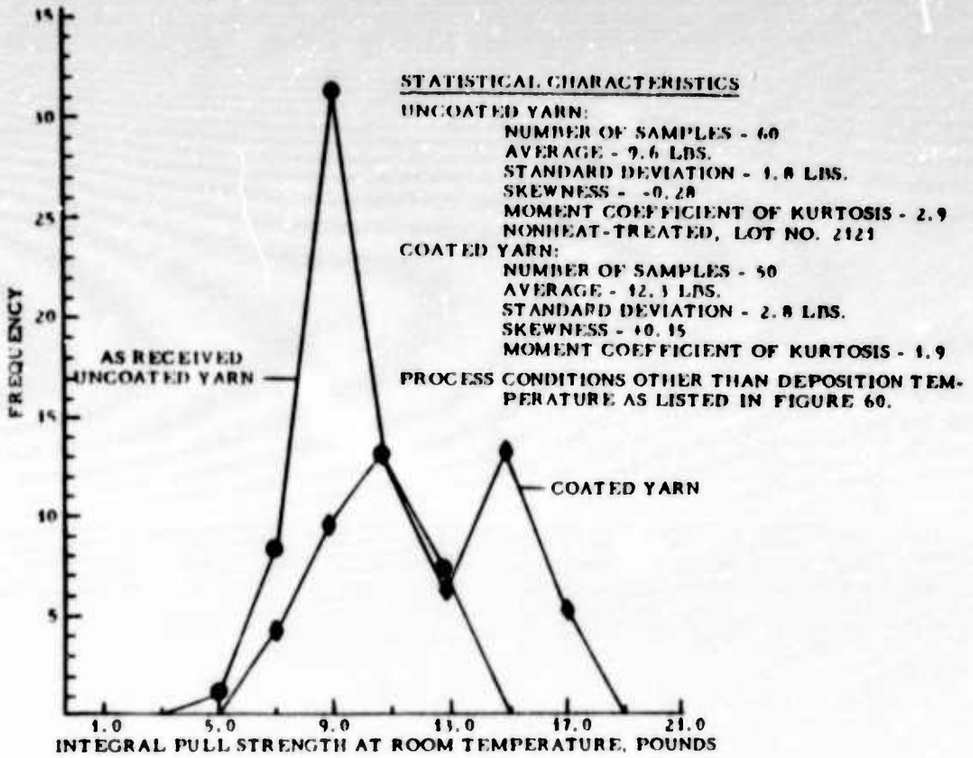


Figure 63. Frequency Polygon Comparison Between As Received Uncoated Yarn and Yarn Pyrolytically Coated at 2100°C

L-319

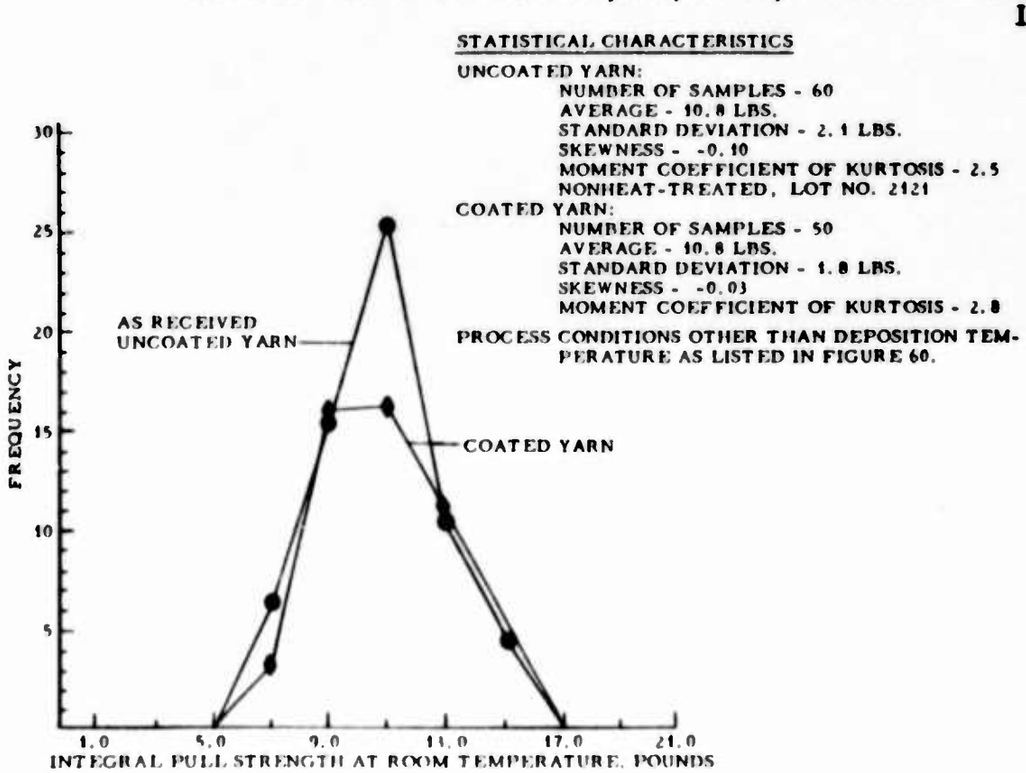


Figure 64. Frequency Polygon Comparison Between As Received Uncoated Yarn and Yarn Pyrolytically Coated at 2200°C

L-320

Contrary to previous experience, the effect of the coating decreased with increasing deposition temperature as shown by Figures 65 to 67. This was the result of coating a yarn which had not been previously heat-treated. Since the yarn had not been stabilized, considerable arcing occurred between the yarn and the contact wheels at temperatures of 2000°C and above. As the temperature was increased, the arc intensity increased until at 2200°C the effect was severe enough to occasionally destroy complete plies. This illustrates the necessity of heat-treating carbon yarn to temperatures approximating those used in the deposition process prior to coating it. In using carbon yarns this should be considered as a normal processing step.

In support of these conclusions, a second series of tests were made using a different lot of carbon yarn which had been heat-treated prior to coating. Once the yarn had been heated to 1900°C, reheating alone had little effect as is shown in Figure 68.

The results of this series are presented in Figures 69 to 72. The yarn strength stayed fairly constant through the temperature range investigated showing only a slight increase in strength as the deposition temperature was increased. These results are more in line with those obtained previously and show that heat-treatment is required to prevent deterioration of the yarn at deposition temperatures in excess of 2000°C.

A plot of the average tenacity ratios for the material in Figures 69 to 72 shows that consistent tenacity gains were made as the result of the pyrolytic graphite coatings. These ratios are presented in Figure 73.

3.7. Final Yarn Processing Conditions

Combining the results of the penetration studies, the vacuo studies and the alternate coating series, a standard set of conditions for coating the rest of the yarn to be used in this contract was established. These conditions were:

1. Pretreat yarn by further carbonization to a temperature of 1900°C by resistance heating in an atmosphere of argon at an ambient pressure of 720 Torr and a yarn speed of 25 ft./min.

2. Apply pyrolytic coating to yarn using resistance heating with Chamber B, at an ambient pressure of 1 atm., a methane concentration of 88 parts per 100 parts of argon by volume, a total argon flow of 34 standard cubic ft./min., and a yarn tension of 90 grams.

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 14.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN./MIN	METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

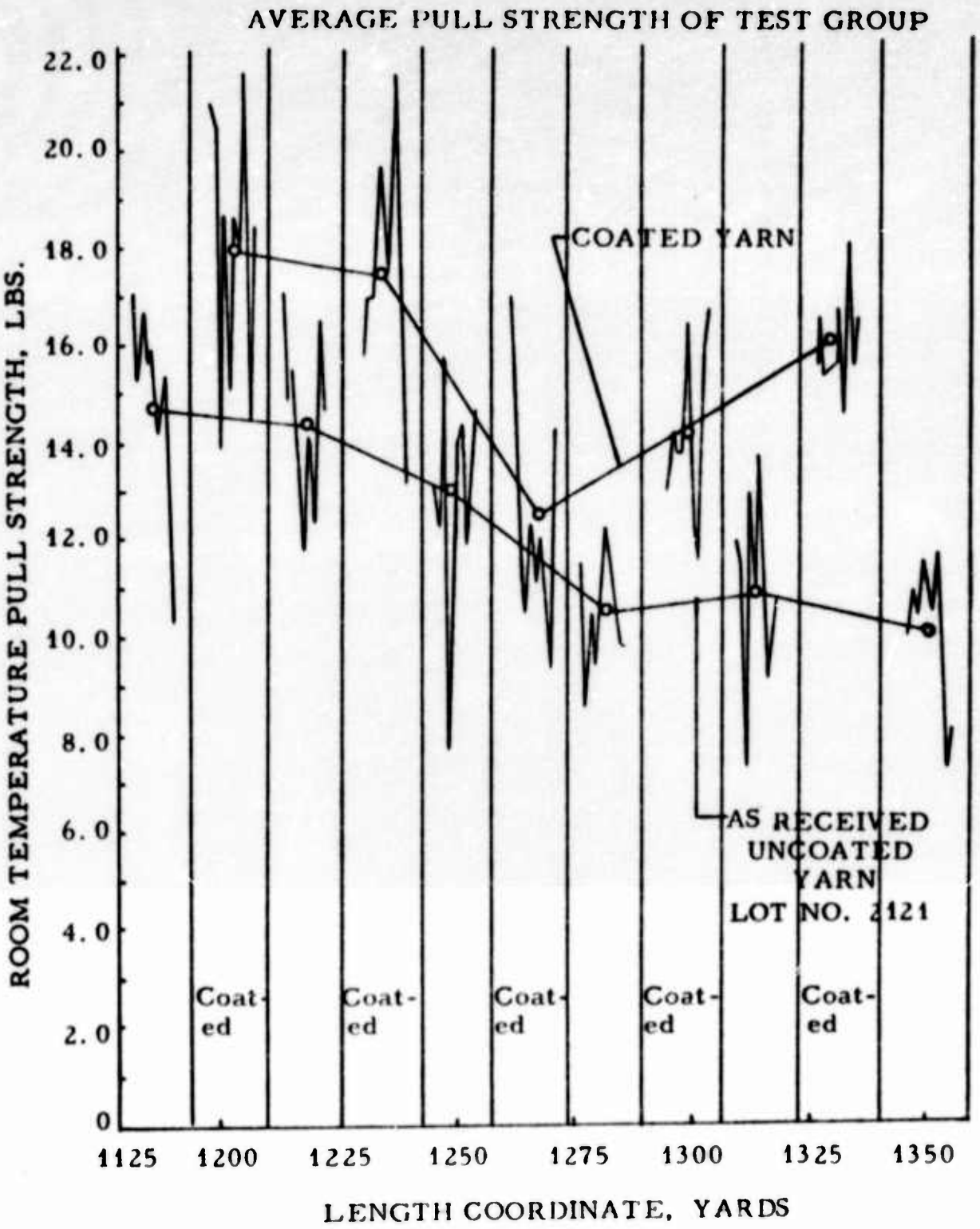


Figure 65. Coating Evaluation, Chamber B, 2000°C

L-1039

Table 52. Data for Figure 65

Yarn Processing History Lot No. 2121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2033	Uncoated				10	2290	14.7	2.9	
2034	2000	25	88	63.4	10	2270	18.0	3.6	1.2
2035	Uncoated				10	2280	14.4	2.9	
2036	2000	25	88	63.4	10	2420	17.5	3.3	1.2
2037	Uncoated				10	2280	13.0	2.6	
2038	2000	25	88	63.4	10	2330	12.5	2.4	1.0
2039	Uncoated				10	2305	10.5	2.1	
2040	2000	25	88	63.4	10	2240	14.2	2.9	1.3
2041	Uncoated				10	2290	10.9	2.2	
2042	2000	25	88	63.4	10	2360	16.1	3.1	1.5
2043	Uncoated				10	2300	10.1	2.0	

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 5-4 YDS	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN./MIN.	METHANE CONCENTRATION	- 60 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

AVERAGE PULL STRENGTH OF TEST GROUP

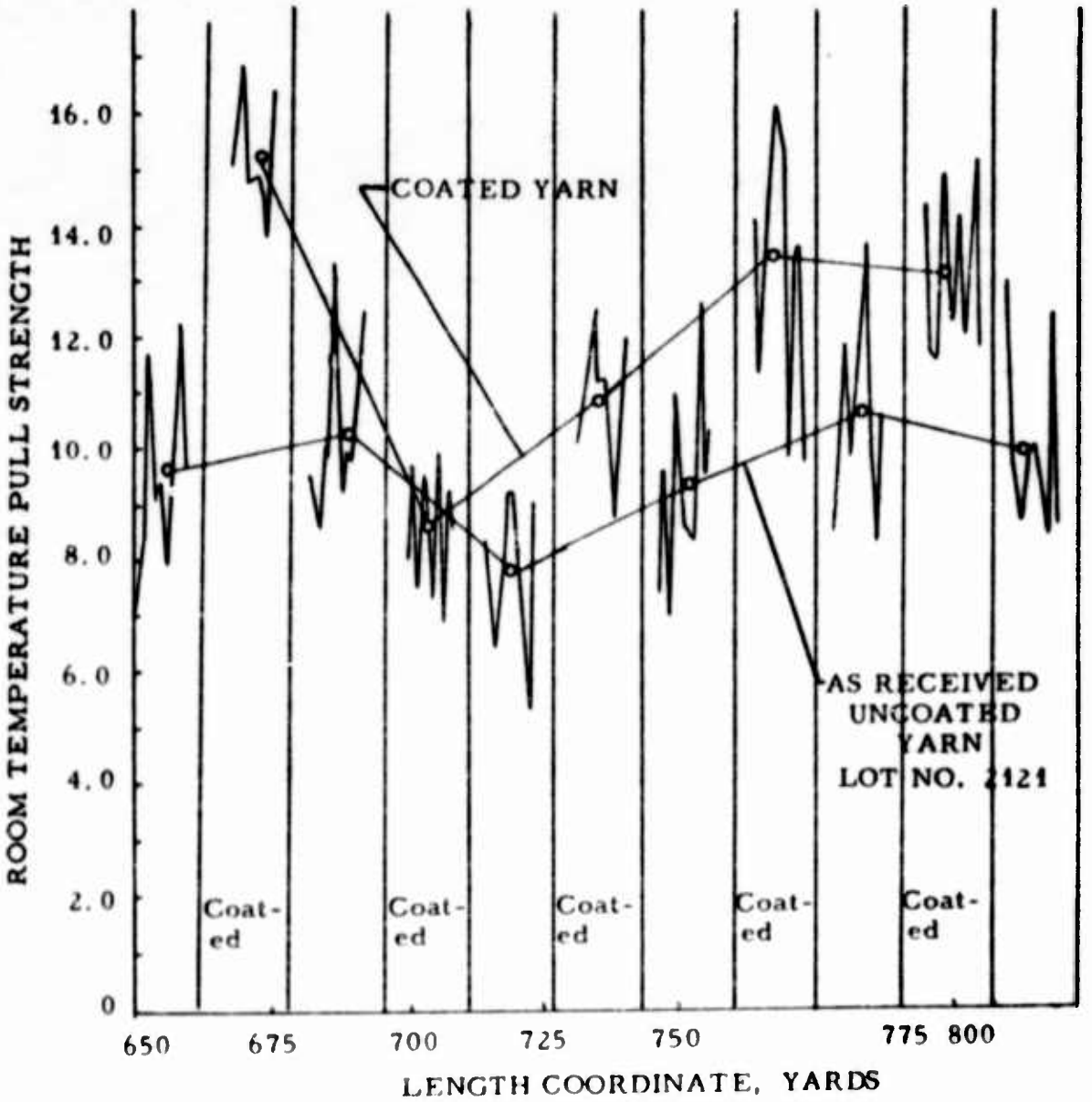


Figure 66. Coating Evaluation, Chamber B, 2100°C

L-1040

Table 53. Data for Figure 66

Yarn Processing History Lot No. 2121									
Expt. No.	Deposition Tem. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2000	Uncoated				10	2220	9.6	2.0	
2001	2100	25	88	63.4	10	2360	15.3	3.0	1.5
2002	Uncoated				10	2230	10.3	2.1	
2003	2100	25	88	63.4	10	2360	8.6	1.7	0.9
2004	Uncoated				10	2300	7.8	1.5	
2005	2100	25	88	63.4	10	2300	10.9	2.2	1.3
2006	Uncoated				10	2300	9.4	1.9	
2007	2100	25	88	63.4	10	2350	13.5	2.6	1.3
2008	Uncoated				10	2300	10.7	2.1	
2009	2100	25	88	63.4	10	2240	13.2	2.7	1.3
2010	Uncoated				10	2300	10.0	2.0	

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT. / MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN. /MIN.	METHANE CONCENTRATION	- 66 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

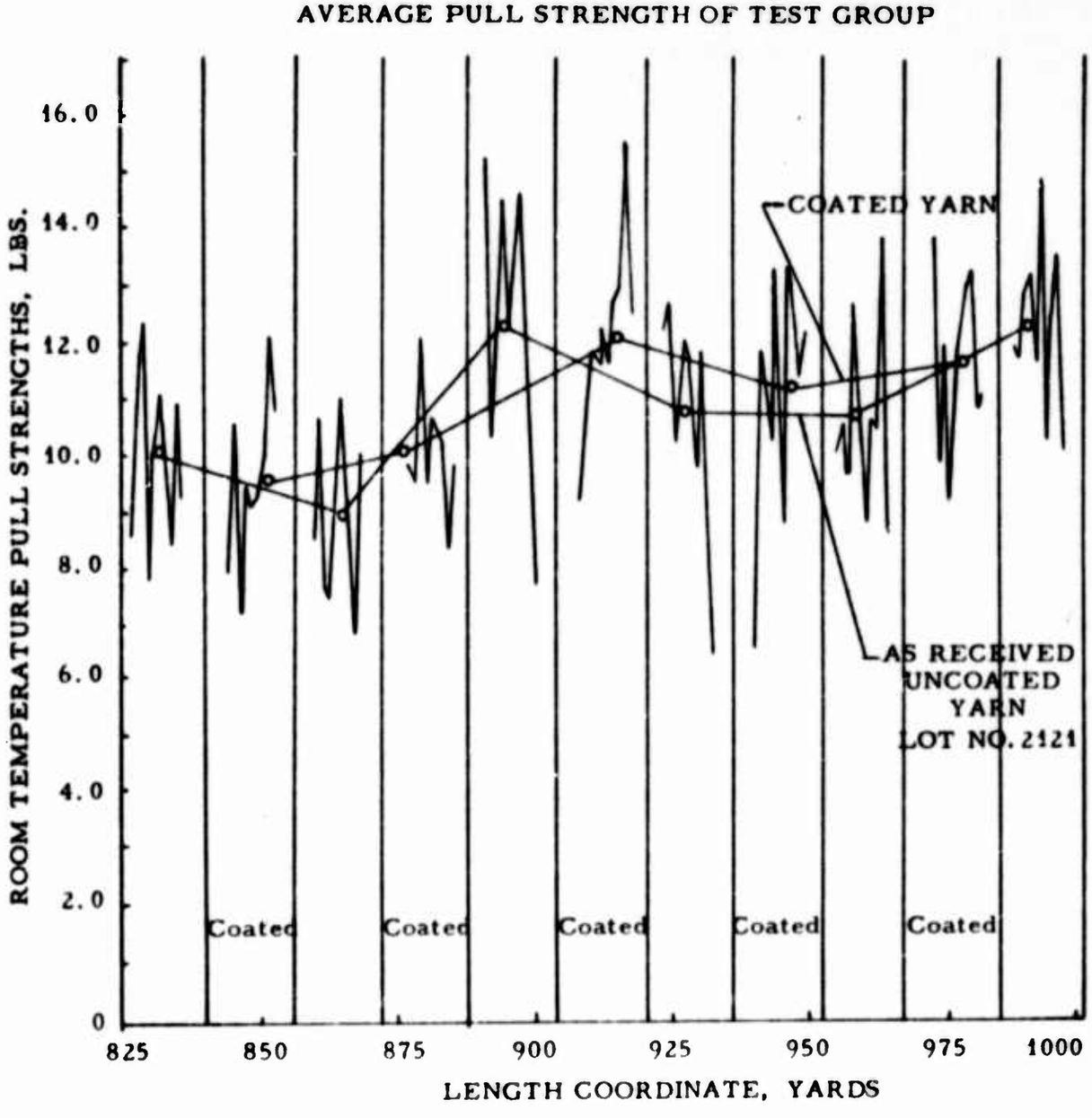


Figure 67. Coating Evaluation, Chamber B, 2200°C

L-1041

Table 54. Data for Figure 67

Yarn Processing History Lot No. 2121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2011	Uncoated				10	2240	10.0	2.0	
2012	2200	25	88	63.4	10	2440	9.5	1.8	1.0
2013	Uncoated				10	2220	8.9	1.8	
2014	2200	25	88	63.4	10	2350	10.0	1.9	0.9
2015	Uncoated				10	2220	12.2	2.5	
2016	2200	25	88	63.4	10	2400	12.0	2.3	1.0
2017	Uncoated				10	2200	10.7	2.2	
2018	2200	25	88	63.4	10	2370	11.1	2.1	1.0
2019	Uncoated				10	2200	10.6	2.2	
2020	2200	25	88	63.4	10	2350	11.6	2.2	1.0
2021	Uncoated				10	2200	12.2	2.5	

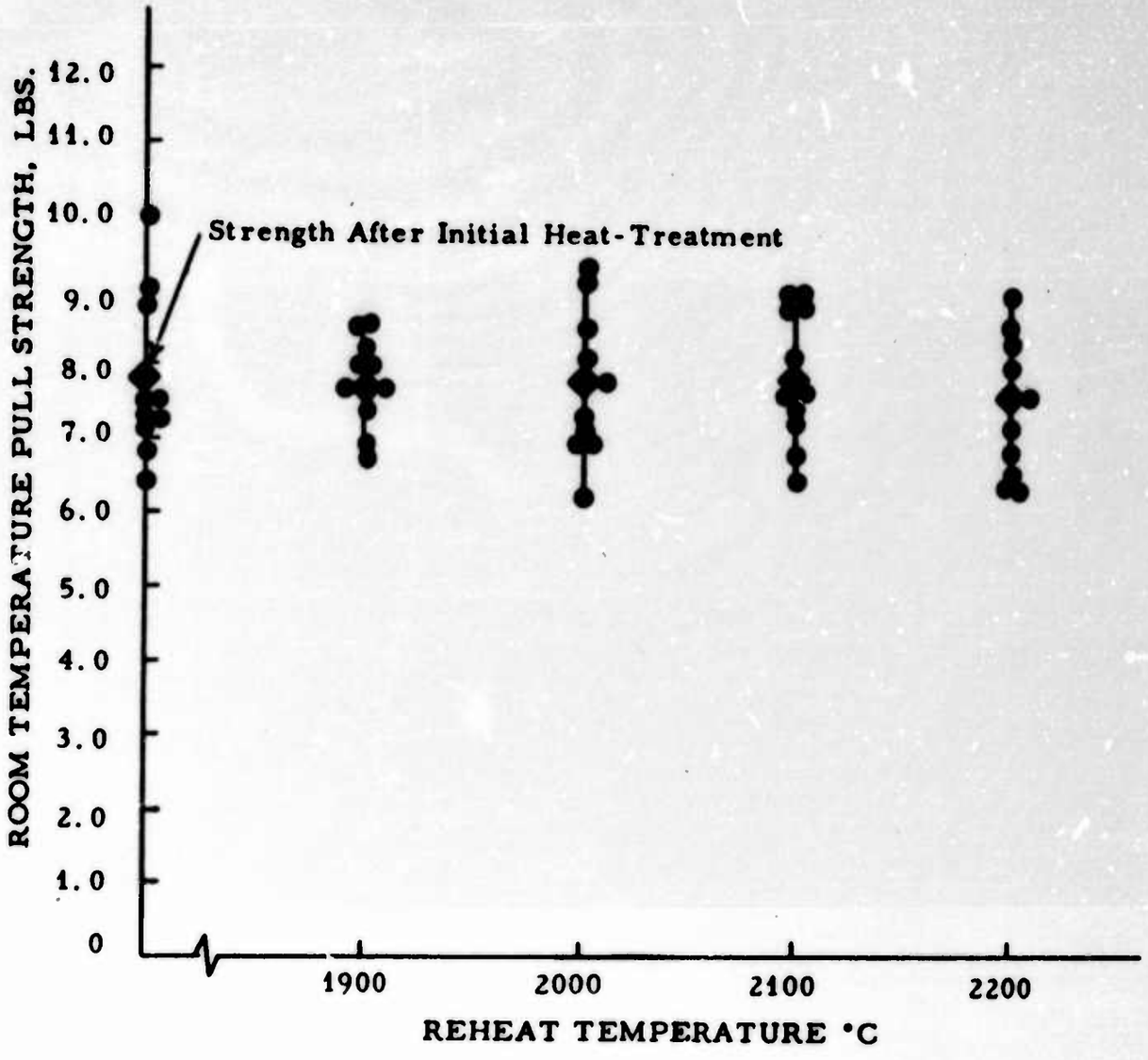


Figure 68. Strength of Heat-Treated Yarn after Reheating in Argon Atmosphere, Resistance Apparatus, Speed 25 Ft./Min.

L-1042

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN./MIN.	METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

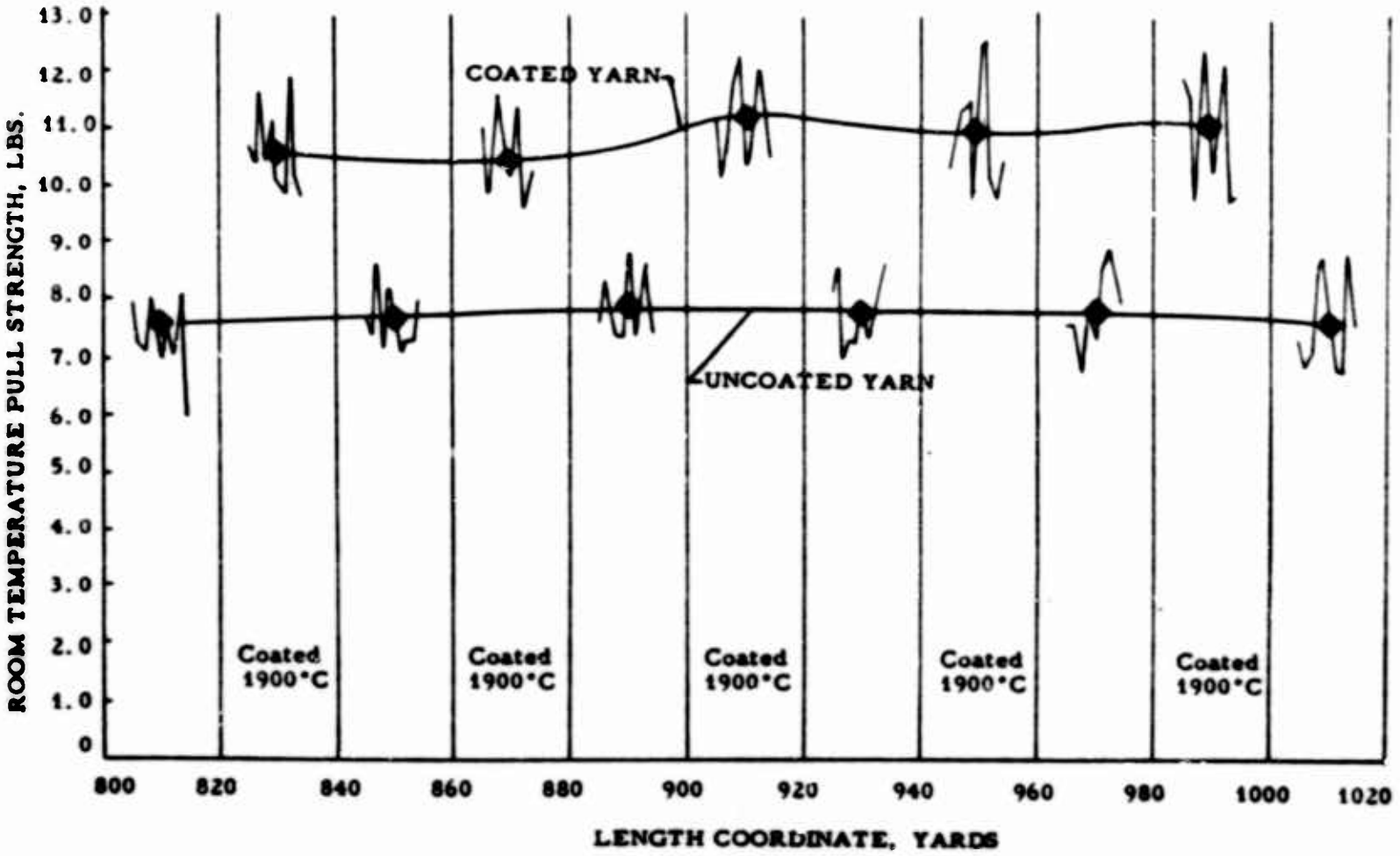


Figure 69. Coating Evaluation of Heat-Treated Yarn by Intermittent Process Application, Chamber B, 1900°C

L-1043

TEST CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.
TEST SPAN	- 4.25 IN.
STRAIN RATE	- 1.0 IN./MIN.
JAW TYPE	- A-2

COATING CONDITIONS	
DEPOSITION TEMPERATURE	- AS NOTED
FILAMENT SPEED	- 25 FT./MIN.
ARGON FLOW	- 34.0 STD. FT.³/HR.
METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
HEATING	- BY RESISTANCE

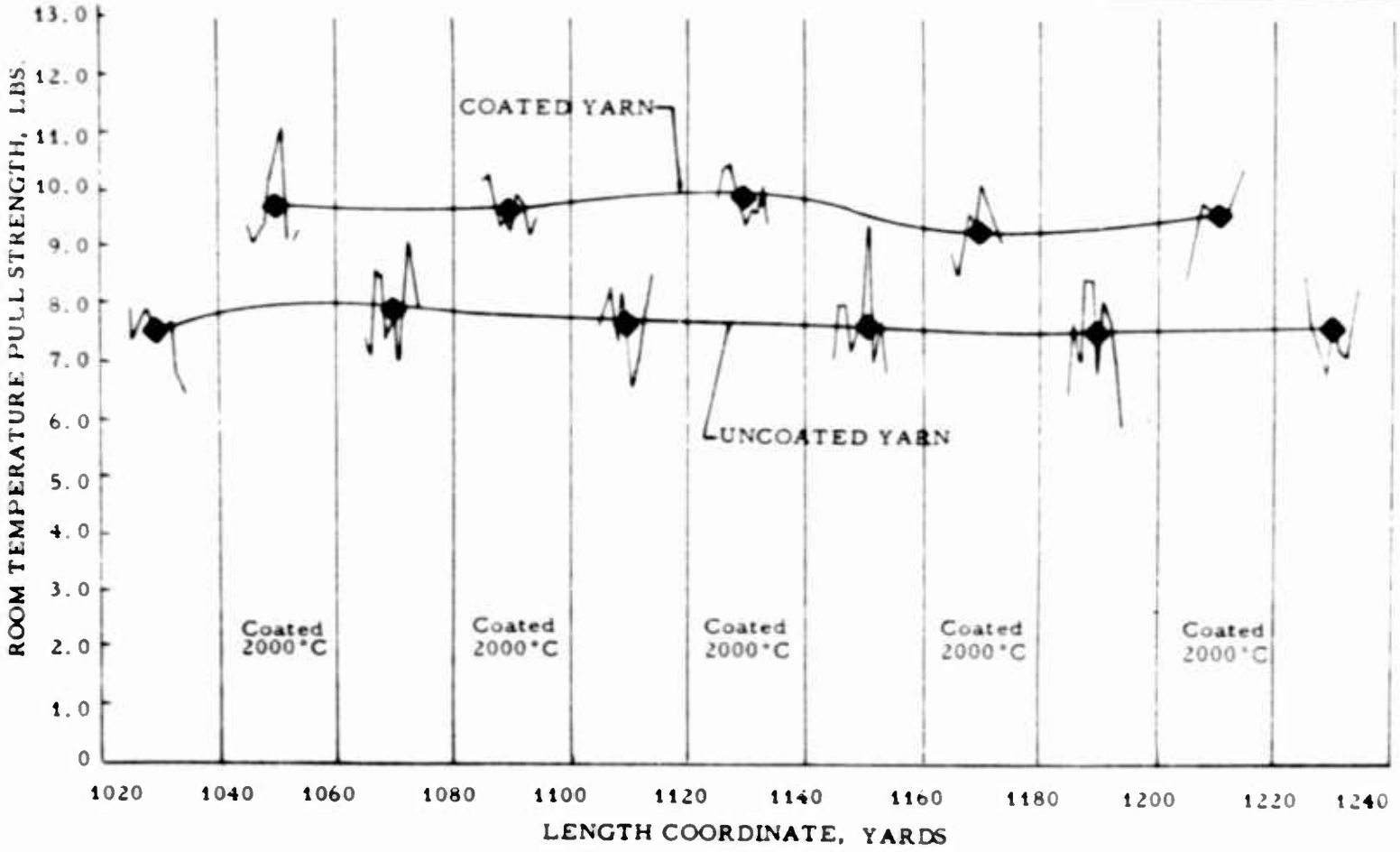


Figure 70. Coating Evaluation of Heat-Treated Carbon Yarn by Intermittent Process Application, Chamber B, 2000°C

L-1044

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN./MIN.	METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

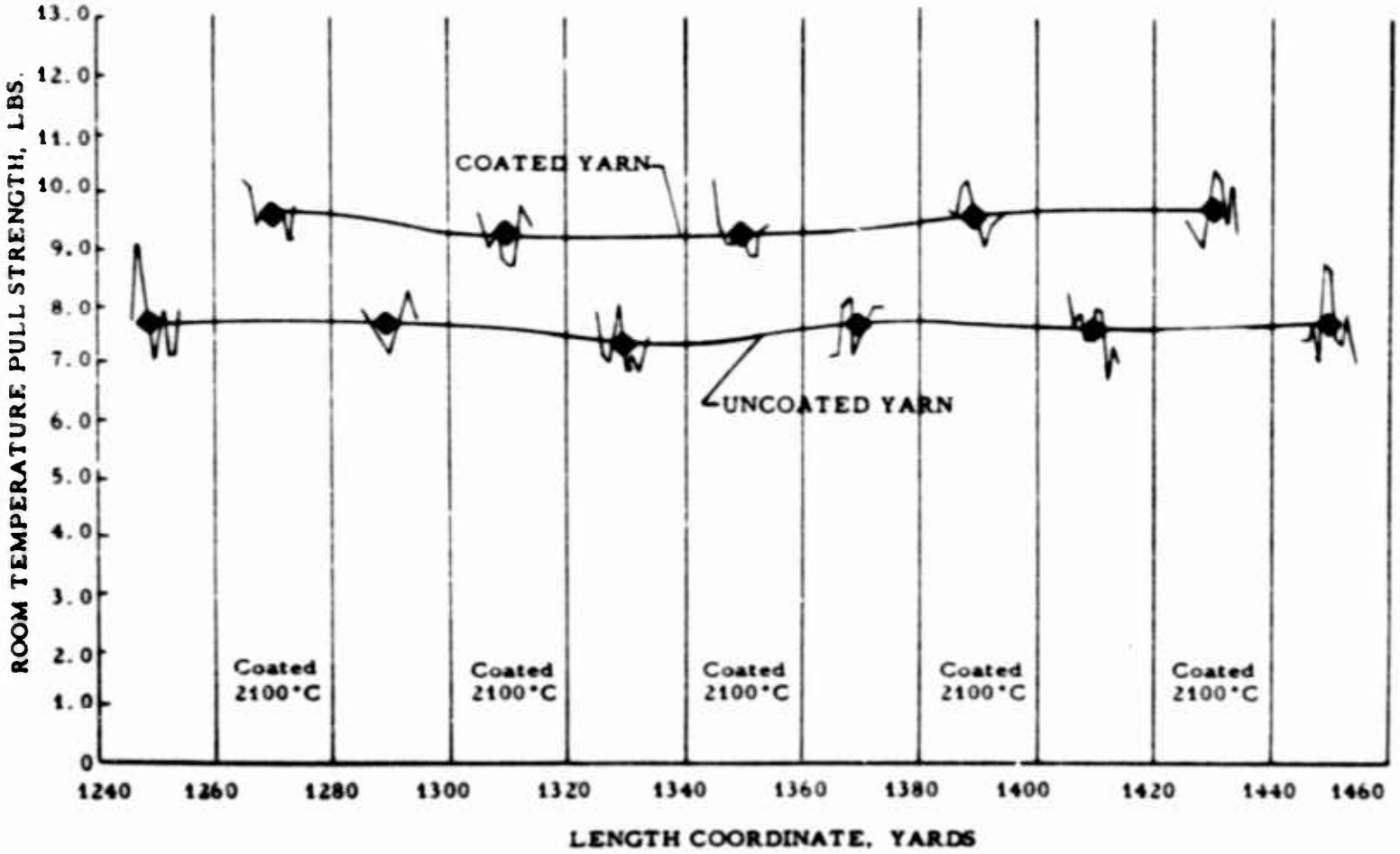


Figure 71. Coating Evaluation of Heat-Treated Carbon Yarn by Intermittent Process Application, Chamber B, 2100°C

L-1045

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.³/HR.
STRAIN RATE	- 1.0 IN./MIN.	METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

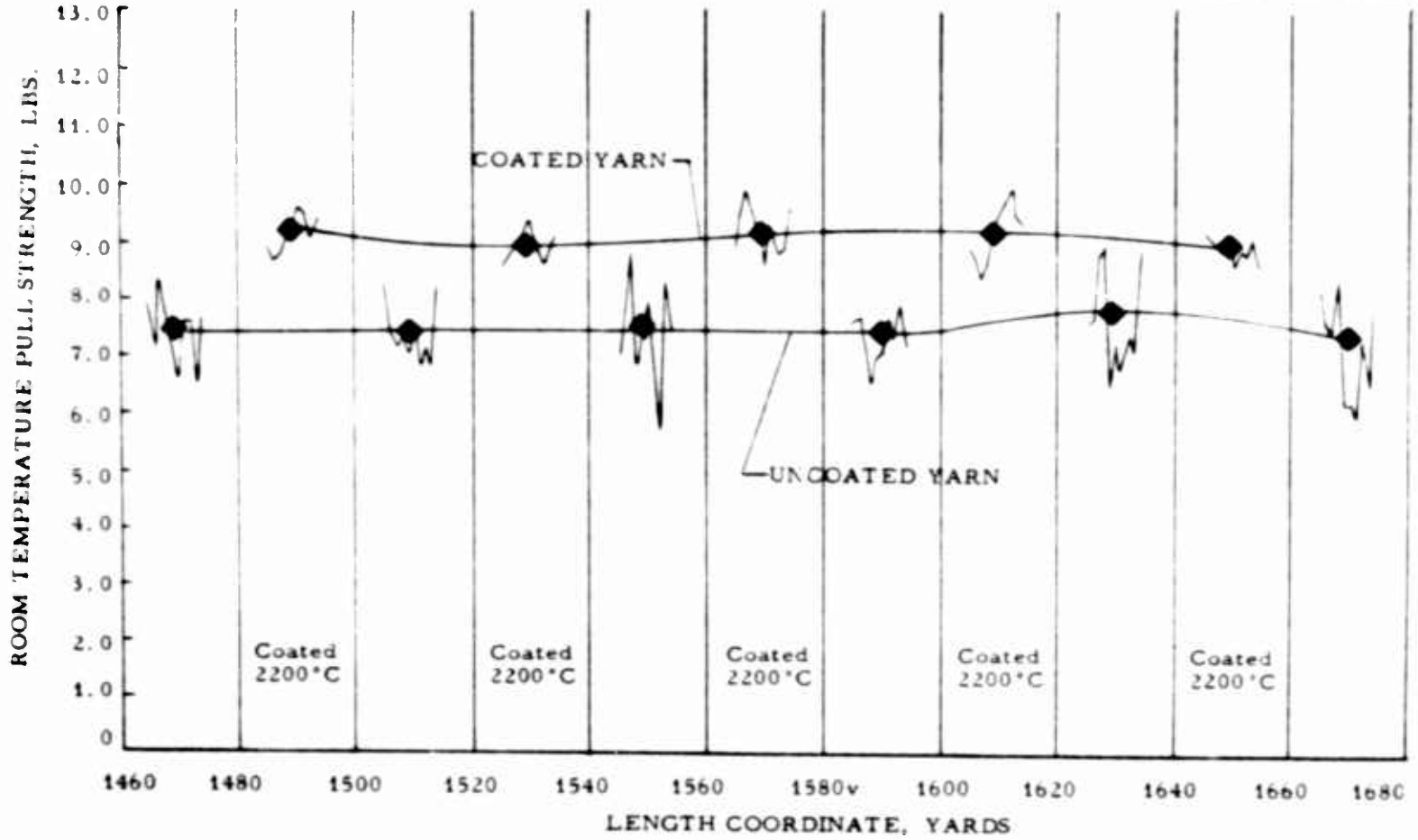


Figure 72. Coating Evaluation of Heat-Treated Carbon Yarn by Intermittent Process Application, Chamber B, 2200°C

L-1046

Table 55. Data for Figure 69

Yarn Processing History Lot No. 1121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2200	Uncoated				10	2230	7.6	1.6	
2201	1900	25	88	63.4	10	2270	10.6	2.1	1.3
2202	Uncoated				10	2235	7.7	1.6	
2203	1900	25	88	63.4	10	2250	10.5	2.1	1.3
2204	Uncoated				10	2255	7.9	1.6	
2205	1900	25	88	63.4	10	2250	11.2	2.2	1.4
2206	Uncoated				10	2225	7.8	1.6	
2207	1900	25	88	63.4	10	2250	11.0	2.2	1.4
2208	Uncoated				10	2240	7.8	1.6	
2209	1900	25	88	63.4	10	2300	11.0	2.2	1.4
2210	Uncoated				10	2230	7.6	1.5	

Table 56. Data for Figure 70

Yarn Processing History Lot No. 1121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2211	Uncoated				10	2220	7.5	1.5	
2212	2000	25	88	63.4	10	2260	9.7	2.0	1.3
2213	Uncoated				10	2260	7.9	1.6	
2214	2000	25	88	63.4	10	2260	9.7	2.0	1.3
2215	Uncoated				10	2230	7.7	1.5	
2216	2000	25	88	63.4	10	2260	9.9	2.0	1.3
2217	Uncoated				10	2225	7.6	1.5	
2218	2000	25	88	63.4	10	2258	9.3	1.9	1.2
2219	Uncoated				10	2210	7.5	1.5	
2220	2000	25	88	63.4	10	2260	9.6	1.9	1.2
2221	Uncoated				10	2210	7.6	1.5	

Table 57. Data for Figure 71

Yarn Processing History Lot No. 1121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000 m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2222	Uncoated				10	2240	7.7	1.6	
2223	2100	25	88	63.4	10	2280	9.7	1.9	1.2
2224	Uncoated				10	2240	7.7	1.6	
2225	2100	25	88	63.4	10	2270	9.3	1.9	1.2
2226	Uncoated				10	2230	7.3	1.5	
2227	2100	25	88	63.4	10	2280	9.3	1.8	1.2
2228	Uncoated				10	2250	7.7	1.5	
2229	2100	25	88	63.4	10	2280	9.6	1.9	1.3
2230	Uncoated				10	2230	7.6	1.5	
2231	2100	25	88	63.4	10	2280	9.7	1.9	1.3
2232	Uncoated				10	2260	7.7	1.5	

Table 58. Data for Figure 72

Yarn Processing History Lot No. 1121									
Expt. No.	Deposition Temp. °C	Yarn Speed Ft./Min.	Meth. Conc. Parts/100 Parts Argon	Total Gas Flow Std. $Ft.^3/Hr.$	No. of Samples	Average Denier g/9000m	Avg. Pull Strength lbs.	Average Tenacity grams/denier	Tenacity Ratio
2233	Uncoated				10	2190	7.4	1.5	
2234	2200	25	88	63.4	10	2350	9.2	1.8	1.2
2235	Uncoated				10	2190	7.4	1.5	
2236	2200	25	88	63.4	10	2340	8.9	1.7	1.1
2237	Uncoated				10	2210	7.5	1.5	
2238	2200	25	88	63.4	10	2370	9.2	1.8	1.2
2239	Uncoated				10	2170	7.4	1.5	
2240	2200	25	88	63.4	10	2360	9.2	1.8	1.2
2241	Uncoated				10	2250	7.8	1.5	
2242	2200	25	88	63.4	10	2360	8.9	1.7	1.1
2243	Uncoated				10	2170	7.4	1.5	

TEST CONDITIONS		COATING CONDITIONS	
SAMPLE INTERVAL WITHIN TEST GROUP	- 36 IN.	DEPOSITION TEMPERATURE	- AS NOTED
DISTANCE BETWEEN TEST GROUPS	- 6-8 YDS.	FILAMENT SPEED	- 25 FT./MIN.
TEST SPAN	- 4.25 IN.	ARGON FLOW	- 34.0 STD. FT.^{3}/HR.
STRAIN RATE	- 1.0 IN./MIN.	METHANE CONCENTRATION	- 88 PARTS/100 PARTS ARGON
JAW TYPE	- A-2	HEATING	- BY RESISTANCE

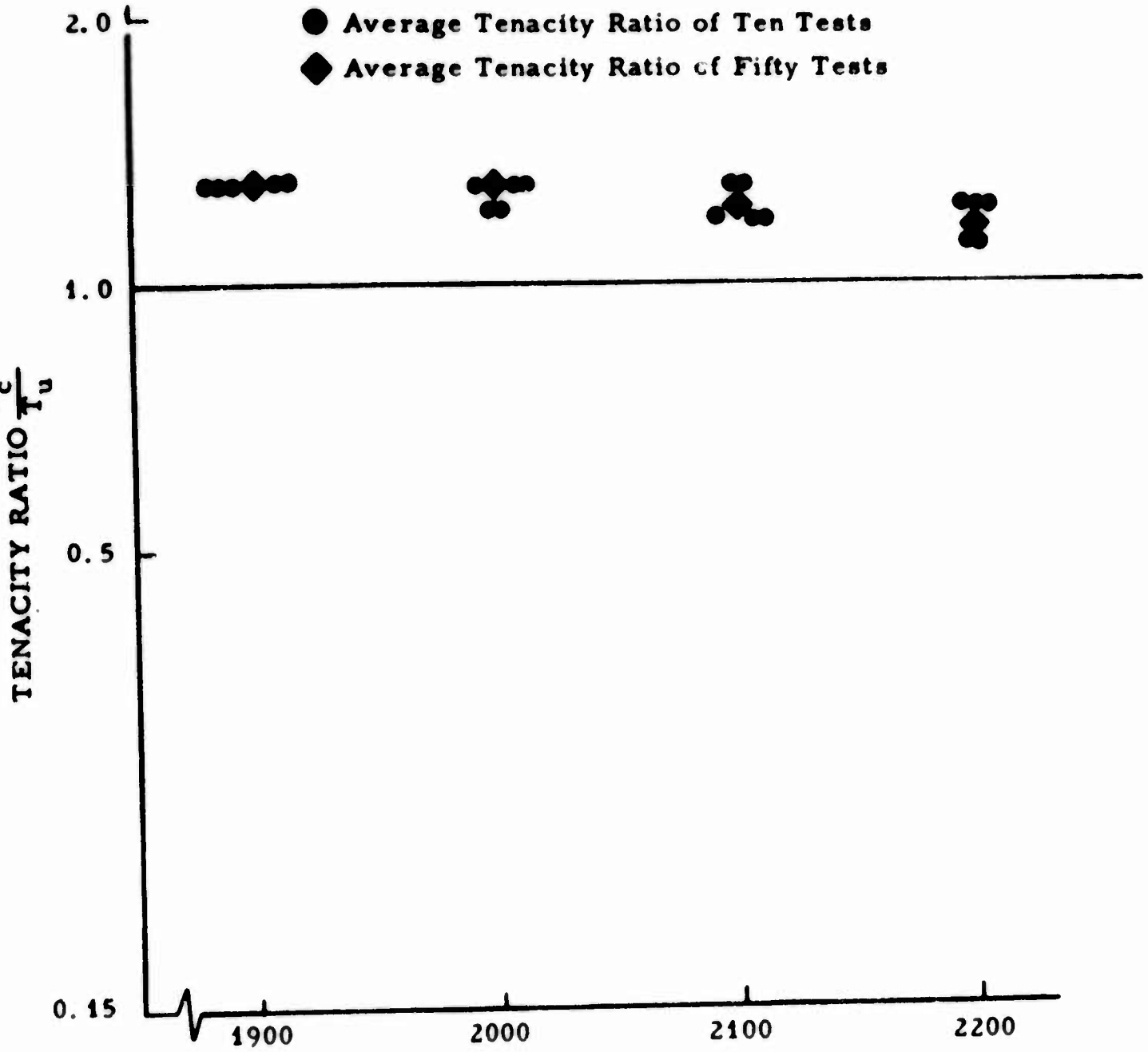


Figure 73. Tenacity Ratio of Heat-Treated Carbon Yarn After Being Coated With Pyrolytic Graphite at Various Deposition Temperatures L-1047

4. PROPERTIES OF SELECTED YARNS

Several physical properties of both coated and uncoated carbon yarn were measured to determine the effect of the pyrolytic graphite coating upon these properties.

The pull strength, which is the force required to break a strand of yarn in tension, was used in combination with the denier to determine the tenacity of the yarn. Since the average pull strengths for all determinations are listed in the tables accompanying each tenacity plot, this discussion will be limited to the methods employed in arriving at an accurate measurement of the pull strength.

Other physical properties measured were the denier, the tensile strength of the individual filaments, the thermal conductivity, the electrical resistance and the relationship between pull strength and twist.

4.1. Pull Strength Determinations

An accurate determination of the pull strength is necessary to determine the tenacity of a yarn. The reliable determination of the pull strength is not simple since carbon yarn, especially when coated with pyrolytic graphite, is not easily gripped without incurring damage to the filaments or the coating.

4.1.1. Standard Instron Method

Initial determinations were carried out with standard textile grips mounted in an Instron Universal testing machine. These grips, shown in Figure 74, are operated pneumatically and have a pretensioning device. After the yarn has been fed into the grips and clamped by the upper jaws, manual prestressing of the yarn closes the lower jaws. Both the prestressing and the clamping force exerted by the jaws can be adjusted over wide ranges.

Figure 74. Standard Textile Grips

With these grips, "jaw breaks" would occur in 90 of 100 tests on coated yarn and in 40 of 100 tests on uncoated material. The term "jaw break" means that the yarn does not fail in the free test section but somewhere in the lengths involved in the clamping. The resulting measurements are not accurate indications of pull strength. The principal points of failure lie both in the jaws and on the curved guide over which the yarn is suspended, as illustrated in Figure 75.

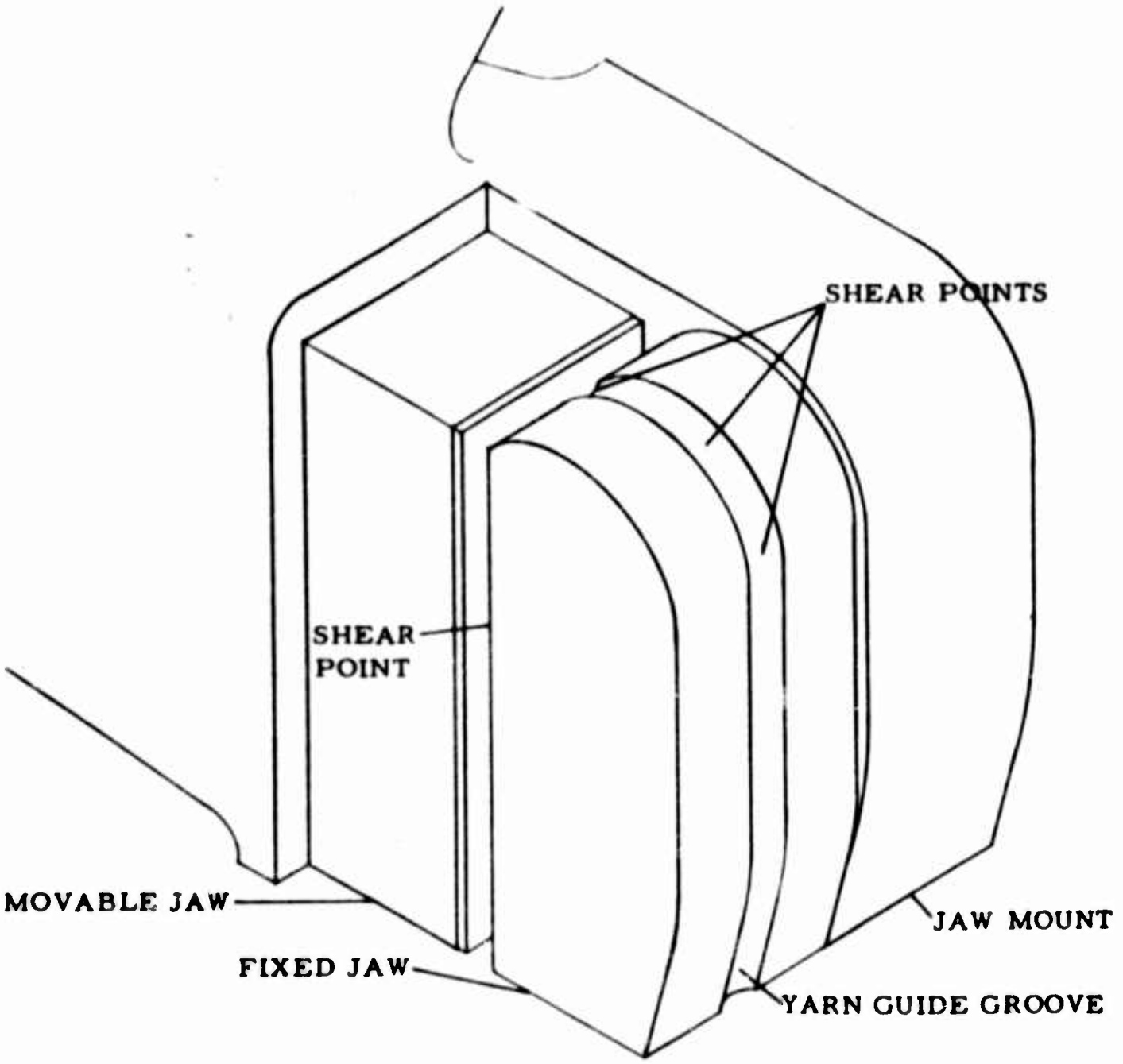


Figure 75. Principal Shear Points for Yarn Tested in Standard Textile Grips L-28

The jaw breaks in the guide are due to the small radius of curvature which creates high shear forces in this area. The breaks occurring in the jaws themselves can be attributed to the crushing action of the clamp since with these jaws, only the static clamping force can be adjusted. A very much higher dynamic force is developed during the act of closing the jaws because of their considerable mass. Apparently, this dynamic force is sufficient to crush individual filaments when they cross each other as they must do in a twisted yarn. Slippage of the yarn within the grips also contributed to the jaw breaks. When the static clamping force was adjusted to the point where no crushing of the filaments occurred, the yarn would slip out of the grips. As stronger yarns were tested, the static clamping force had to be increased to eliminate slippage in the grips and this caused further damage to the filaments. These problems could not be eliminated so this method was discontinued.

4.1.2. Modified Instron Method

While an investigation into clamping devices was being conducted, a temporary device was used to test the pull strength of the yarn. This setup consisted of a system of large pulleys as illustrated in Figure 76.

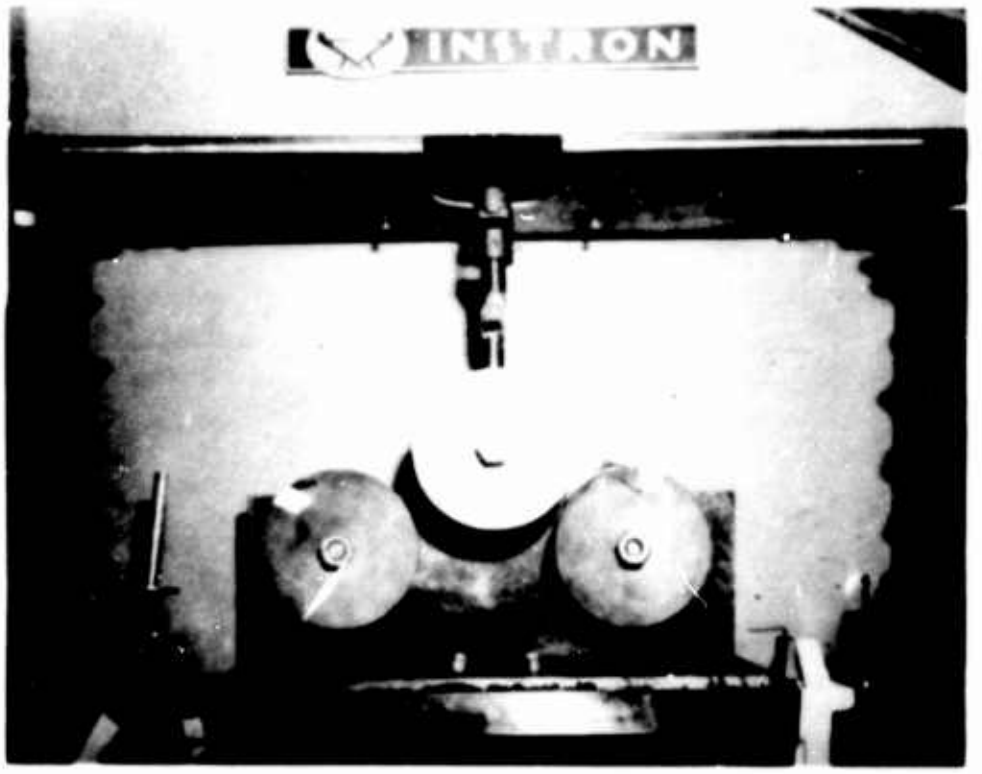


Figure 76. Modified Instron Pull Strength Assembly

In this setup, two pulleys were fixed to the movable cross member of the Instron and fastened so that they were unable to turn. A third pulley, mounted on the fixed cross member of the Instron, was attached so that

it was free to rotate. The yarn was then wrapped around one of the fixed pulleys, passed over the movable pulley and wrapped around the other fixed pulley. When the stress was applied, friction of the yarn against the fixed pulleys was the holding force. Only those breaks which occurred between the points of tangency were considered valid. The use of this equipment gave unacceptable breaks less than 15 per cent of the time. This system was used during the chamber design and process variables determinations.

4.1.3. Scott Testing Machine

A third approach to determining the pull strength of the yarn utilized the Scott testing machine, model X-3, shown in Figure 77. Tests of various types of standard clamps such as the Spino Cord, Jute Association, Callaway, Fletcher, and Spruance, revealed that only the A-2 clamp shown in Figure 78 would consistently give satisfactory breaks. The grips on these clamps are closed by screws which eliminate impact effects and the clamps are faced with rubber to decrease slippage and crushing effects. This machine gives less than 1 per cent jaw breaks and was used for all final yarn evaluations, as well as for evaluation of materials woven from both coated and uncoated yarns.

4.2. Denier Determinations

The denier of the yarn is the weight in grams of a section 9000 meters long. The denier measurements were made by determining the weight of 3 to 10 samples each 1 meter long, averaging those weights and multiplying this number of 9000. Within a given lot of yarn, the denier measurements were found to be quite uniform.

4.3. General Characteristics of Yarns Used in Property Determinations

All of the coated yarns characterized in this section were prepared under the conditions listed in Section 3.7 The coated material was prepared from heat-treated yarn with deposition temperatures as listed in the individual topics.

Since the coating conditions determine the quality and thickness of the coating on the yarn, the values given for tensile strength, electrical resistance and thermal conductivity, should be considered as typical only for yarn prepared as specified.

4.4. Tensile Strength at Room Temperature

Tensile strength measurements at room temperature were made on 24 individual filaments. Eight samples were taken from the carbon yarn as it was received, eight from a section which had been heat-treated to 1900°C, and the remaining eight from the coated yarn. For the coated yarn, the processing conditions were as described in Section 3.7 with a deposition temperature of 2200°C.

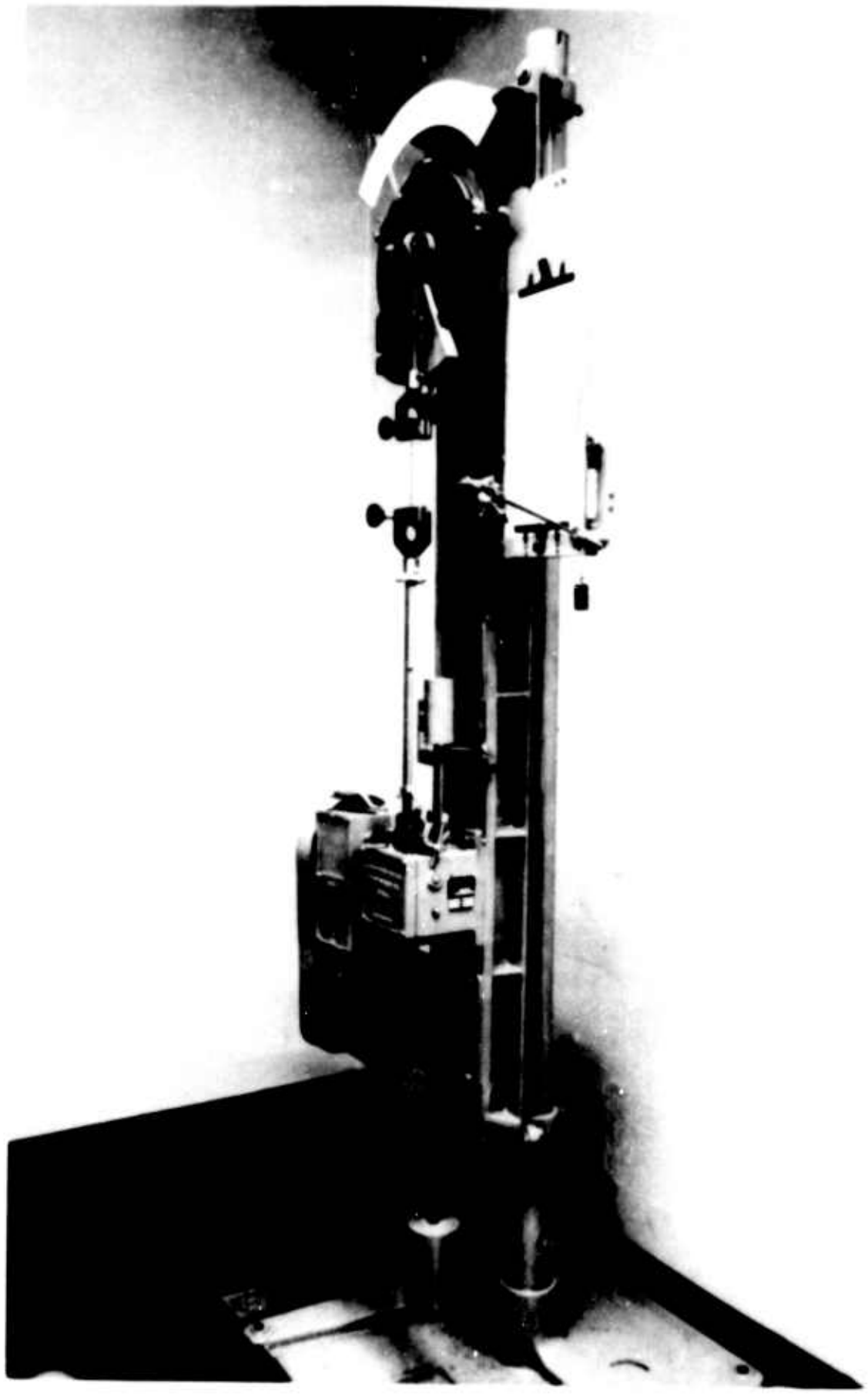


Figure 77. Scott Testing Machine, Model X-3

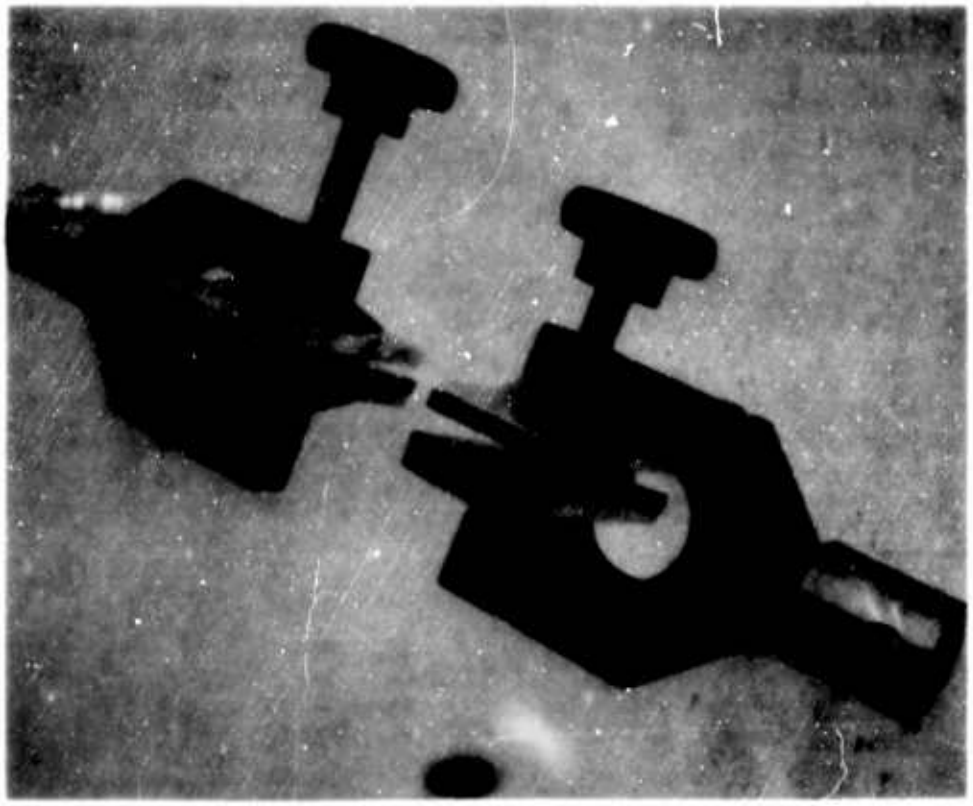


Figure 78. A-2 Clamps

The force measurements were made at the Carbon Products Division Research Laboratory, Parma, Ohio in a special machine developed for whisker studies. The filament cross sections were determined by microscopic techniques. The results are shown in Table 59. The tensile strength of pyrolytically coated filaments was 40 per cent higher than that of the as received carbon yarn, and 50 per cent higher than that of the heat-treated yarn.

The cross section of a typical coated filament was shown in Figure 59. Using the ratio of the area of coating to that of the core (0.50), combined with the strength data shown in Table 59, we can calculate that the strength of the coating alone must be greater than 200,000 lbs./in.^{2}. This value is much higher than has been reported for commercial pyrolytic graphite with a thickness of $\frac{1}{8}$ inch and above[2] where room-temperature values in the order of 20,000 lbs./in.^{2} are the rule.

Any attempt to fully exploit this strengthening effect of the pyrolytic coating on the fiber will require a determination of the modulus of elasticity of the pyrolytic graphite deposited at various temperatures. Since many of the properties of the pyrolytic graphite are greatly affected by the deposition temperature, it is reasonable to expect that the elastic modulus may also be affected. If this were the case, it might be possible to adjust the modulus of the coating to produce an extremely strong composite filament.

Table 59. Tensile Strength of As Received, Heat-Treated and Pyrolytically-Coated Carbon Filaments

Material Lot No. 212103-1	Test No.	Breaking Force grams	Area 10^{-7} cm^2	Tensile Strength lbs./in.^{2}	Average lbs./in.^{2}	Standard Deviation, lbs./in.^{2}
Uncoated Carbon Filaments As Received	1	5.09	7.27	100,000	92,000	18,000
	2	4.28	6.02	101,000		
	3	5.90	8.82	45,000		
	4	7.60	8.92	121,000		
	5	6.99	9.83	101,000		
	6	6.16	10.48	84,000		
	7	4.55	11.38	57,000		
	8	4.55	8.49	76,000		
Uncoated Carbon Filaments Heat-Treated at 1900°C	1	6.82	8.80	110,000	86,000	21,000
	2	3.77	8.25	65,000		
	3	2.65	4.27	88,000		
	4	4.00	7.74	73,000		
	5	3.78	8.49	63,000		
	6	3.24	7.51	61,000		
	7	5.90	8.20	102,000		
	8	6.44	7.43	123,000		
Pyrolytically Coated Carbon Filaments	1	7.08	7.01	144,000	129,000	27,000
	2	7.29	7.01	148,000		
	3	5.44	9.86	78,000		
	4	5.70	6.31	128,000		
	5	9.43	7.70	174,000		
	6	7.33	8.21	127,000		
	7	8.44	9.06	132,000		
	8	6.00	8.52	100,000		

4.5. Electrical Resistance at Room Temperature

A series of measurements was made to determine to what extent the pyrolytic coating process changed the electrical resistance of the yarn. The results of these measurements are shown in Table 60. The electrical resistance at room temperature of coated yarn is given as a function of the deposition temperature and compared to the resistance of as received uncoated yarn. The as received uncoated yarn was heated directly to the temperature desired without prior 1900°C treatment. The coating process lowered the resistance of the yarn by as much as 44 per cent.

Table 60. Room-Temperature Electrical Resistance of Uncoated and Coated Yarn

Temperature T °C	Electrical Resistance at Room Temperature, ohms/inch	
	Uncoated Yarn Heated to Temperature T	Yarn Pyrolytically Coated* at Nominal Temperature T
1900	6.4	4.6
2000	6.2	3.8
2100	5.9	3.5
2200	5.7	3.2
* Coating conditions in Section 3.7		

4.6. Thermal Conductivity

In several applications of carbon yarn, thermal conductivity is expected to be a major factor. Therefore, efforts were made to determine the effect of the pyrolytic coating process on this property.

All measurements were made on cylindrical bundles of yarn filaments in the longitudinal direction. Both uncoated and coated yarn were evaluated. The coated material was processed under the conditions described in Section 3.7 at a deposition temperature of 1900°C.

4.6.1. Room-Temperature Measur ments

At room temperature, measurements were conducted in steady state by determining the temperature difference between two points of a carbon yarn bundle of known cross section. The yarn bundle was mounted between a heat source and a heat sink in the bell jar of a high-vacuum

apparatus. The heat sink is kept at 30°C by an isothermal bath while the heat source is an electrical heater of known power input. The heat source was operated at 100°C. A mean thermal conductivity over the 30° to 100°C temperature range was measured in this manner which may be considered as approximately a room-temperature value.

The results are shown in Table 61 in which values for ATJ graphite are included for comparison. The pyrolytic coating increases the room-temperature thermal conductivity of the filaments by a factor of 2.3, but the absolute value is still low compared to ATJ graphite.

Table 61. The Longitudinal Thermal Conductivity of Uncoated and Coated Carbon Filaments at Room Temperature

Material Lot No.		Thermal Conductivity, cal./sec.$^{-1}$ cm^{-1} °K^{-1} Room Temperature
Uncoated Carbon Filaments		0.064
Pyrolytically Coated Carbon Filaments		0.145
ATJ Graphite	Parallel to the Grain	0.28
	Across the Grain	0.21
Deposition Temperature: 1900°C		

4.6.2. High-Temperature Measurements

At elevated temperature, a transient method was used to measure the thermal conductivity. In an argon atmosphere, one flat end of a cylindrical carbon yarn bundle was subjected to arc image radiation until equilibrium was established between absorption and loss of heat. The arc image radiation was interrupted and the rate of cooling of the previously irradiated surface was recorded electronically. This cooling rate with the density and specific heat of the sample was used to compute the thermal conductivity.

Since the data reported in the Quarterly Progress Report dated February 29, 1964 was obtained, improvements have been made in the method of measurement. Hence the data given in Table 62 is to be considered more accurate and reliable than that previously reported.

4.7. Effect of Twist on Pull Strength

Yarns coated under this contract consisted of five strands, twisted 1.1 to 1.3 turns per inch. Since twist is known to affect the pull

Table 62. The Longitudinal Thermal Conductivity of Uncoated and Coated Carbon Filaments at 2100°C

		Thermal Conductivity, cal./sec.$^{-1}$ cm^{-1} °K^{-1}
		2200 (± 150)°C
Uncoated Carbon Filaments		0.032
Pyrolytically Coated Carbon Filaments		0.031
ATJ Graphite	Parallel to the Grain	0.10
	Across the Grain	0.08
Deposition Temperature: 1900°C		

strength of normal textile materials, it was necessary to investigate this relationship for both coated and uncoated carbon yarns.

Yarn samples 10 inches in length were mounted in a Suter Twist Tester as shown in Figure 79, untwisted to zero turns per inch, retwisted to various degrees, and subsequently broken. Using this procedure pull strength data were obtained for twists between zero and 2.1 turns per inch.

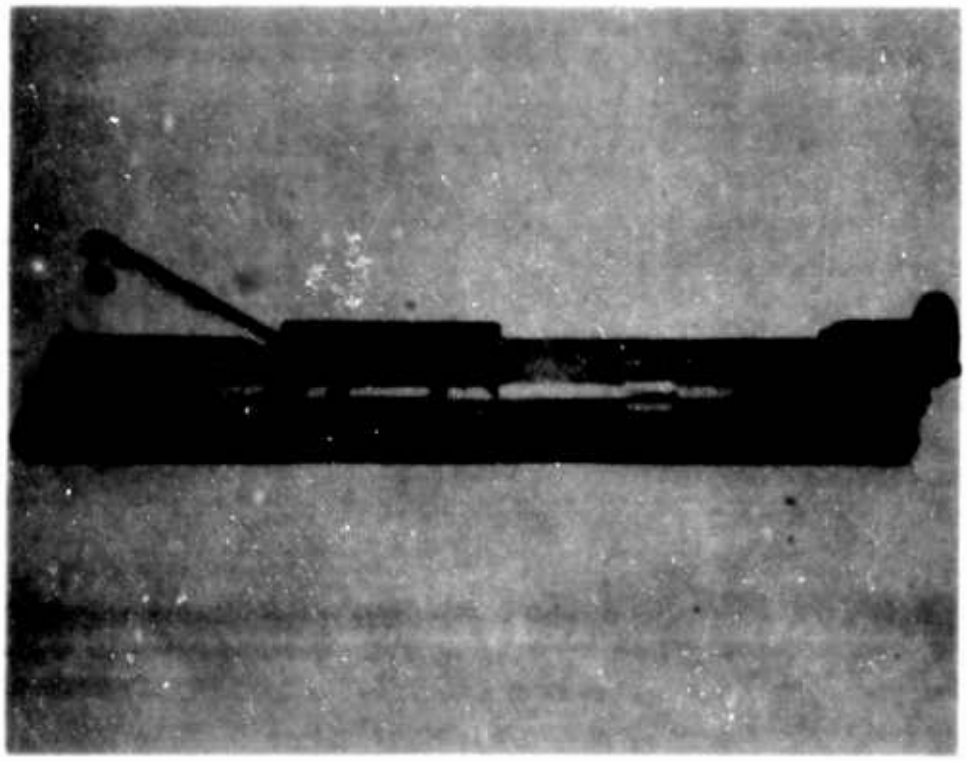


Figure 79. Suter Twist Tester

The results compiled in Table 63 reveal that highest strength is obtained at the original twist of the carbon yarn. Any twist level, other than the original, evidently disturbed the form into which the filaments used as raw material were frozen during their carbonization. Apparently, this introduced detrimental stresses. Taylor, et al,[3] have shown that for synthetic fibers improved pull strength should generally be expected as the twist level is increased; however, according to these results, to be of benefit, twist changes would have to be made prior to carbonization and preferably in the manufacture of the basic fiber.

Table 63. Effect of Enforced Twist Levels on Uncoated and Pyrolytically Coated Yarn

Enforced Twist Level, $inch^{-1}$	Integral Pull Strength*), lbs.	
	Carbon Yarn Original Twist: 1.3 $inch^{-1}$	Pyrolytically Coated Yarn**) Original Twist: 1.1 $inch^{-1}$
0.0	9.8	12.5
0.2	11.4	10.8
0.4	9.4	12.5
0.6	10.2	11.3
0.8	7.8	12.6
1.0	10.2	14.8
1.1	--	14.8
1.2	12.8	--
1.3	12.2	14.8
1.5	12.6	13.6
1.7	--	13.0
1.9	--	11.5
2.1	--	12.4

*) Average of two tests:
**) Coating Conditions of Section 3.6. (1900°C)

5. BULK MATERIALS DEVELOPMENT

As the final phase of the work under this contract, the pyrolytically coated yarns were fabricated into representative composites and tested. A portion of the coated yarn was woven into cloth tape and then incorporated, by conventional techniques, into a laminate composite. A second portion of the coated yarn was chopped into short lengths and processed into a macerate or nonplanar composite.

Analogous products were prepared from the uncoated heat-treated yarn to provide a basis for comparison.

5.1. Woven Tape

Coated and uncoated yarns were woven into tapes, $\frac{1}{2}$ and $1\frac{1}{2}$ inches wide, containing 16 warp coils per inch. The weaving was done by the Bally Ribbon Mills of Bally, Pennsylvania. To determine the effect on strength of the degree of curvature the yarn undergoes in various types of weaves, we tried two patterns, the square and basket weaves, illustrated in Figure 80.

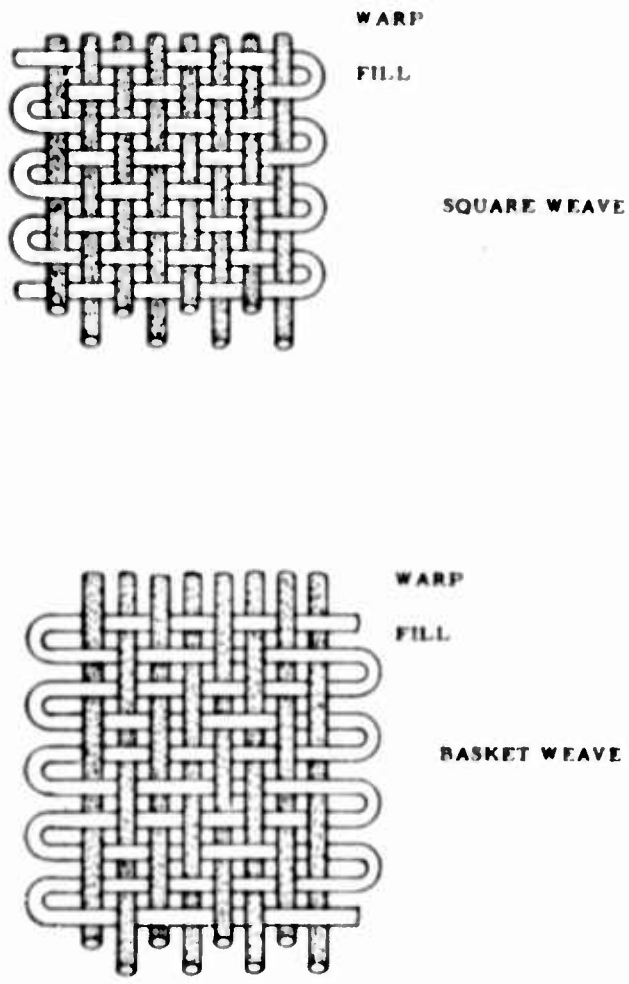
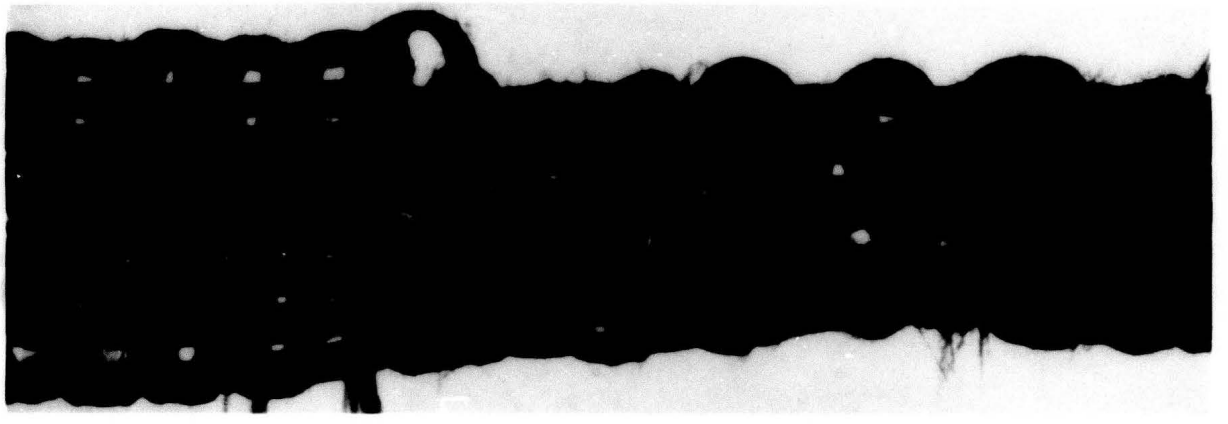


Figure 80. Square and Basket Weaves Used for Tape Manufacture L-1048

The yarn coated with pyrolytic graphite was well-suited for weaving. The coating acted as a "sizing" which allowed the yarn to move through the loom without being frayed. The uncoated material could not be woven without the application of a glutinous sizing agent. Even after being sized, it still presented serious difficulties. Some of the "weaving mishaps" are shown in Figure 81. There were no such problems with the coated yarn.

(Tape from coated yarn)



(Weaving mishap in tape from uncoated yarn)

Figure 81. Comparison of Tapes Produced from Coated and Uncoated Yarns

The tapes were evaluated by determining the "load distribution factor." The load distribution factor is the ratio of the actual longitudinal tape strength to the theoretical longitudinal (warp) strength. The theoretical strength is determined by multiplying the pull strength of a single warp strand by the number of warp ends.

For both types of weave, the material woven from the coated yarn had a strength of 100 pounds per inch of width which corresponds to a load distribution factor of 0.7. The strength of the uncoated material was 81

pounds per inch which gave a load distribution factor of 0.63. The superior weavability of the coated yarn is reflected in the strength characteristics of the tape.

More recently, changes in fabrication techniques which include using a stiffer yarn as the warp material have resulted in tapes made from coated materials which had an average strength of 140 pounds per inch of width, giving load distribution factors of 0.8 to 0.9. For normal textile material this factor is approximately 0.8 which indicates that the coated carbon yarn can be woven as efficiently as commercial textiles.

5.2. Composite Materials

The coated yarns were incorporated into fibrous composites to compare the material with uncoated yarns as a reinforcing filler. The tapes were used to prepare laminate composites. Yarns were chopped into short lengths and the filaments separated before they were molded into macerate composite.

5.2.1. Laminate Composites

The laminate composites are formed by stacking layers of cloth impregnated with furane-phenolic resin in a frame and curing under pressure. Under the prior contract, Beasley, et al,[4] introduced the graphite cloth-resin concept into graphite technology and their forming methods were adopted for our work. Under their program, the cured composites were carbonized to temperatures up to 3000°C. The product is a composite of carbon filaments in a carbon matrix.

The amount of binder required for the composite is primarily a function of the curing pressure which determines the amount of resin squeezed out of the stack. The binder level is also dependent on the physical characteristics of the filler.

The earlier work[4] indicated that the strongest composites with the carbon cloth used were formed using curing pressures between 150 and 200 lbs./in.^{2}. Figure 82 shows the pronounced strength maximum obtained as the forming pressure is varied.

The composite prepared from coated yarn at a curing pressure of 150 lbs./in.^{2} had a low flexural strength. Since in the time available only a brief look at the effect of curing pressure was possible, a much higher forming pressure was tried. Although the properties of the composite were improved, the curing pressure and binder level were not optimum. The composite made from the coated material at 500 lbs./in.^{2} curing pressure appears to be binder poor which prevents the development of superior properties in the composite. The composite made from the uncoated material did not appear to be binder deficient.

Further work would be required to develop the proper processing for this material.

5.2.2. Macerate Composites

Short lengths of chopped filaments are used as reinforcement in the macerate composites. The chopped filaments are mixed with a resin

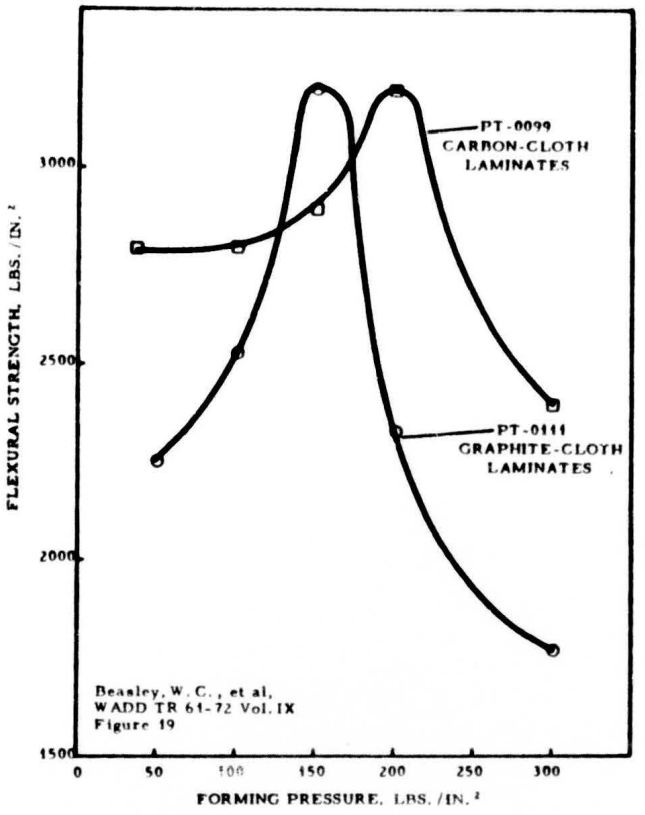


Figure 82. Curing Pressure, Strength Relation for Laminates L-256

Table 64. Characteristics of Laminates Prepared From Woven Yarn

Laminate Base Material	Curing Pressure lbs./in.²	Density of Graphitized Product g/cc	Average Flexural Strength* lbs./in.²
Tape as woven from coated yarn, square weave	150	1.31	1489
Tape as woven from coated yarn, square weave	500	1.01	2367
Tape as woven from uncoated yarn, square weave	500	0.99	2817

*Average of 3 samples as determined under the following conditions:

Sample size: $\frac{1}{4}$ x $\frac{1}{4}$ x 5 inches
Third-point loading
Loading Rate: 0.02 in./min.
Loading forces perpendicular to layer planes

binder, and the composite is formed and cured by conventional hot molding techniques.

An evaluation of macerates using coated and uncoated yarn as raw materials, yields more basic information than the same evaluation of laminates. In laminates, the bonding characteristics between layers is largely influenced by the structure of the woven tape. In macerates, however, the mechanical effect is eliminated and only the surface of the filaments and its compatibility with the binder decides how strong the bulk material will be. Any beneficial or detrimental effect of a pyrolytic coating on the filaments should be more easily detectable in macerates than in laminates.

A few macerate samples were prepared in order to find out whether any obvious differences in binder acceptance existed between coated and uncoated filaments.

Both uncoated and coated yarns were chopped into segments $\frac{1}{4}$ inch long. A cutter of the type shown in Figure 83 was used. A conventional shredder could not be used since its crusing action would damage the pyrolytic graphite coating. The segments were mixed with furane-phenolic resin and molded into macerate composites using Beasley's procedures.

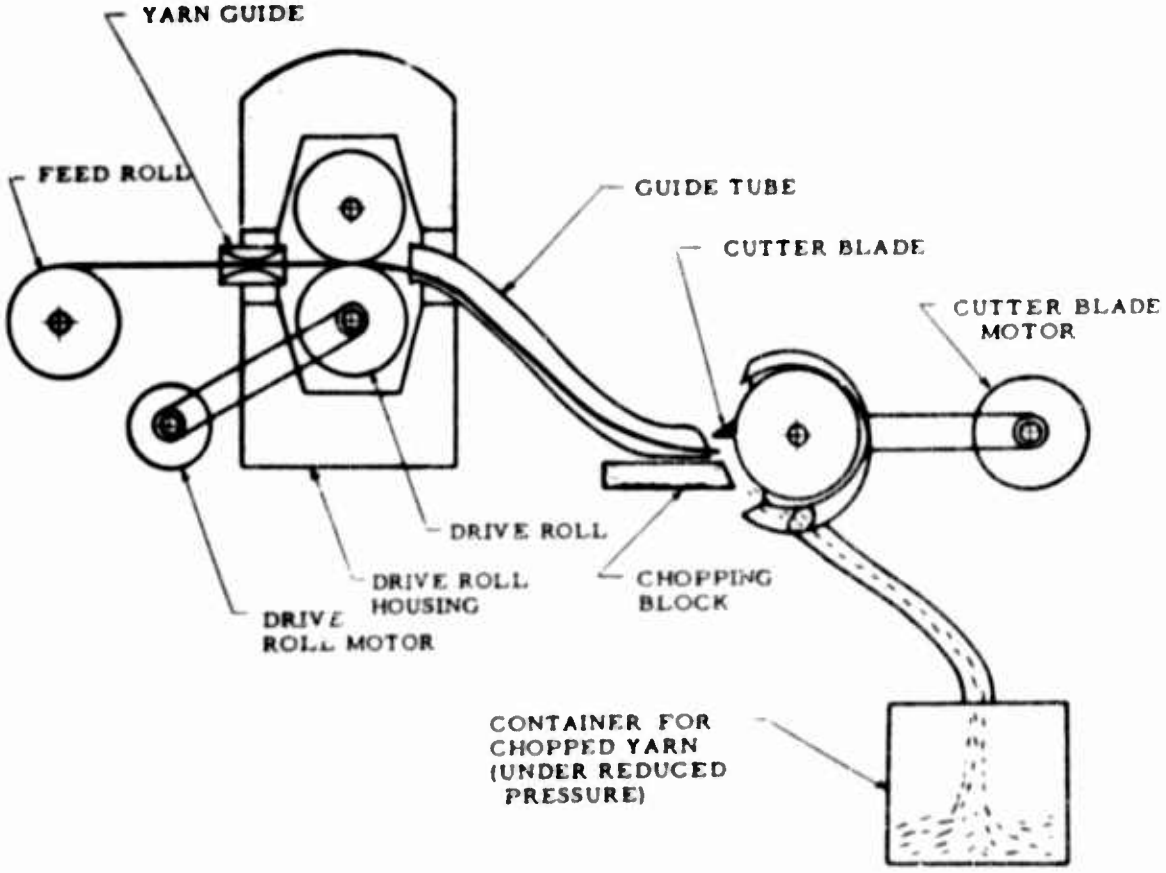


Figure 83. Yarn Chopping Apparatus L-1049

The results in Table 7 show the superiority of coated filaments as a reinforcing filler. For identical binder levels and identical processing conditions, the flexural strength obtained using coated filaments as reinforcing filler was 58 per cent higher than for the uncoated material. The difference in strength of the two composites results not only from a difference in the fiber strength but also from a dissimilar interaction between the filament and the binder. Microscopic examination of the two composites show that the pyrolytic graphite coating may be acting as a coupling agent between the binder and filaments.

Table 65. Characteristics of Macerates Prepared From Chopped Yarn

Macerate Base Material	Binder Level Per Cent	Curing Pressure, lbs./in.^{2}	Density g/cc	Flexural Strength* lbs./in.^{2}
Uncoated Yarn	33.3	2000	0.75	1408
Coated Yarn	33.3	2000	0.84	2221

* Average of 3 samples as determined under the following conditions:

Sample Size: ½ x ½ x 3½ inches
Third-point loading
Loading Rate: 0.02 in./min
Loading forces parallel to the direction of molding

6. RECOMMENDATIONS FOR FUTURE WORK

The carbonized yarn coated with pyrolytic graphite shows an average increase in tenacity over uncoated yarn of at least 30 per cent. This means then that the increased strength-to-weight ratio makes these filaments highly desirable for forming shapes by filament winding of the yarn over a mandrel. Fabrication of articles by this technique would create high strength materials capable of withstanding the temperature extremes found in aerospace applications. It is recommended then that the program be extended to include the study of fabrication of filament wound articles.

Pyrolytic graphite is known to be a good thermal conductor along the a - b axis and an excellent insulator through the c axis. These properties hold true also for the carbon yarn coated with pyrolytic graphite. Such yarns have a much higher room-temperature thermal conductivity along its length than noncoated carbon yarns. These properties can be utilized to good advantage by providing a mechanism for directing heat flow within an article. Proper orientation of the filaments in a material would cause heat to be conducted to a specific point or in a specific direction while acting as a thermal insulator in the direction normal to the heat flow. Filaments could also be selectively dispersed in a matrix such as propellants to provide uniform burning surfaces and preheating of the propellant to promote faster ignition, thereby increasing the burning rate. It is recommended then that the program be extended to include the fabrication of directive thermal flow materials and the study of ignition propagation in solid propellants.

Among the more promising uses of the filaments is their use as reinforcing agents. Present studies indicate that bonding between filaments and binder materials is increased when pyrolytic graphite coatings are placed on the filaments. The pyrolytic graphite tends to act as a coupling agent promoting good bonding of the filaments to the binder material which then makes maximum use of the strength of the reinforcing fibers. Present composites are composed of incompletely bonded fibers which allows less than maximum theoretical strengths to be obtained in composite articles. Therefore, it is recommended that the study of binder systems and bonding phenomena be extended to include determination of optimum forming conditions and binder levels in the fabrication of both laminate and macerate materials using carbon filaments coated with pyrolytic graphite.

In conjunction with the above recommendations a study of the elastic modulus of carbon yarns and of pyrolytic graphite deposited at various temperatures should be made. This, combined with the determination of the strain at failure of the materials, would allow selective fabrication of composites. By carefully controlling the ratio of the elastic modulus and strain at failure of the filaments to that of the binder, high strength composites can be fabricated. It is recommended that a study be made of the modulus of elasticity of pyrolytic graphite, the modulus of the carbon yarn, and the strain at failure of both materials.

As improved carbon yarns become available, the processing conditions for coating such yarns with pyrolytic graphite may change. This would be especially true if different base materials are used to form the carbon yarn or if filaments are of markedly different diameter than those employed in this investigation. It is recommended, therefore, that basic coating process development be refined and/or extended to include these materials.

In summary, therefore, the following areas are recommended for investigation in a continuation of the program:

1. Filament winding in conjunction with suitable binders.

2. Fabrication of directive heat flow material and promotion of uniform and increased burning of solid propellants.

3. Fabrication of laminate and macerate materials from carbon cloth and yarn coated with pyrolytic graphite to utilize the total fiber strength in the composite material.

4. The effect of pyrolytic graphite as a coupling agent to promote resin filament compatibility and load transmission to the filaments.

5. The determination of the modulus of elasticity and strain at failure of pyrolytic graphite deposited at various temperatures as well as the elastic modulus and strain at failure of the carbon yarn.

6. Continued coating process development to refine present processes and to apply to new or different types of carbon yarn.

7. REFERENCES

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